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The report gives results of laboratory and pilot studies of the treatability of wastewaters generated by the manufacture of the pesticides maneb, oryzalin, atrazine, and MSMA. Wastewaters were characterized for pesticide content, routine parameters, and toxicity to fish, algae, and activated sludge organisms. Biological treatability was evaluated in terms of ability of pilot activated sludge systems (1) to successfully operate on a mixture of municipal and pesticide wastewaters and (2) to remove the pesticide and other toxic materials. Ability of activated carbon to treat the wastewaters was determined in adsorption isotherm tests and in granular activated carbon column tests. Study results showed that atrazine, oryzalin, and maneb wastes could be treated successfully with activated carbon, although such treatment had high cost potential. Oryzalin waste disrupted biological treatment. Atrazine and MSMA waste did not disrupt biological treatment, but pesticide concentration was not reduced by biological treatment. Maneb concentrations were reduced by biological treatment, but additional work is needed to determine the fate of breakdown products from the biological treatment of maneb wastewaters.

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Results of studies showed that atrazine, oryzalin and maneb wastes could be treated successfully with activated carbon, though treatment in this fashion had high cost potential. Oryzalin waste disrupted biological treatment. Atrazine and MSMA waste did not disrupt biological treatment but pesticide concentration was not reduced by biological treatment. Maneb concentrations were reduced by biological treatment but additional work is needed to determine the fate of breakdown products from the biological treatment of maneb wastewaters.

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CONVERSION FACTORS

To Convert from	to	Multiply by
Foot^2 (ft^2)	Meter^2	0.0929
Gallons per day (gpd)	Liter per day	3.79
Gallons per minute per foot^2 (gpm/ft^2)	Liter per minute per meter^2	40.796
Pound/1000 gallon (lb/1000 gal)	Gram per liter	0.115
Million gallons per day (mgd)	Liter per day	3.79×10^6

LIST OF ABBREVIATIONS

AS - Activated sludge.
BOD - Biochemical oxygen demand.
CA - Cacodylic acid.
COD - Chemical oxygen demand.
DO - Dissolved oxygen.
DSMA - Disodium methanearsonate.
ETD - Ethylene dithiocarbamate disulfide.
ETM - Ethylene thiuram monosulfide.
ETU - Ethylene thiourea.
GAC - Granular activated carbon.
GC/ECD - Gas chromatography/electron capture detection.
GC/MS - Gas chromatography/mass spectrometry.
gpd - Gallons per day.
I_{14} - % Inhibition of growth of treated algae, compared to control at 14 days.
i.d. - Inside diameter.
LC_{50} - Lethal concentration 50% kill.
LD_{50} - Lethal dose 50% kill.
LDL - Lowest published lethal dose.
MAA - Methanearsonic acid.
μM - Micro-molar.
MLSS - Mixed liquor suspended solids.
MSMA - Monosodium methanearsonate.
ODFS - Optical density full scale.
ppb - Parts per billion (by weight).
ppm - Parts per million (by weight).

LIST OF ABBREVIATIONS (Cont'd)

SS	-	Suspended solids.
TDS	-	Total dissolved solids.
TKN	-	Total Kjeldahl nitrogen.
TLC	-	Thin layer chromatography.
TOC	-	Total organic carbon.
TP	-	Total phosphorus.
TS	-	Total solids.
UV-VIS	-	Ultraviolet-visible.
v/v	-	Volume per volume.
X/M	-	Weight of pesticide adsorbed per weight of carbon.

SECTION 1

INTRODUCTION

In March 1977, Research Triangle Institute (RTI) was requested by the Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP) of the U. S. Environmental Protection Agency (EPA) to conduct laboratory and pilot studies of the treatability of pesticides manufacturing wastewaters. Specifically, the project was addressed to two tasks:

(1) Characterization of pretreatment technology needs.

(2) Development of dynamic carbon sorption data.

The objective of the first task was to develop performance data and design data for biological treatment of actual pesticides manufacturing wastewaters to assist EPA in setting realistic standards for effluents from pesticides manufacture. The manufacturing wastewaters were characterized for their pesticide content and for routine wastewater parameters, including toxicity to fish, algae, and activated sludge. They were then subjected to bench-scale continuous activated sludge (AS) treatment. Biological treatability of wastewaters was evaluated in terms of the ability of AS systems to (1) successfully operate on a mixture of municipal wastewaters and pesticide wastewaters and (2) remove the pesticide and other toxic materials in the wastewaters.

The objective of the second task was to develop dynamic carbon sorption data for actual pesticide manufacturing wastewaters. Ability of activated carbon to treat the wastewaters was determined in adsorption isotherm tests and in granular activated carbon (GAC) column tests. Performance was measured by (1) analysis of pesticide and related compounds before and after treatment and (2) bioscreening of the influent and effluent.

Pesticide analyses were conducted using procedures appropriate for the specific pesticides. These procedures included gas chromatography/mass spectrometry (GC/MS), fluorescence, scanning densitometry, thin layer chromatography, ion chromatography, ultraviolet and visible spectrophotometry, and gas chromatography/electron capture (GC/EC).

Additional objectives in both tasks included compilation of relevant data on the chemistry, health and ecological effects, environmental fate, biological treatability, and physical-chemical treatability of pesticides, particularly those investigated in this project.

In all these studies, requests were made for samples typical of the effluent from a single manufacturing process, i.e., from production of a single pesticide. This sampling approach was chosen to increase the interpretability of data, to aid in isolation of factors which could contribute to problems in treating combined plant effluent, and to facilitate general application of the findings to all plants producing the particular pesticide. The studies were in no way intended to be site-specific, i.e., directed toward characterization and treatment of the combined plant effluent, generally representing wastewaters from a variety of pesticide and non-pesticide manufacturing processes, from a single manufacturer.

Wastewaters for the study were selected after consultation with the project officer and representatives of the National Agricultural Chemicals Association. Factors influencing selection were (1) potential for continued use of pesticide, i.e., those pesticides highly likely to be banned were not considered; (2) production of a significant liquid waste stream; (3) large annual production and widespread use; (4) chemical class, i.e., representatives of several types of chemical structures were selected; (5) availability of the wastewater, i.e., interest of the manufacturers in cooperating with the study.

Pesticide wastewaters were obtained from the manufacture of atrazine, oryzalin, maneb, and MSMA. Atrazine, a herbicide, is ranked Number 1 in terms of production in the triazine category as well as among herbicides in general. The estimated 1974 production was 49.4×10^3 metric tons (Archer *et al.*, 1978). MSMA is ranked Number 1 in the organoarsenical and organometallic category with an estimated 1974 production of 15.9×10^3 metric tons (Archer *et al.*, 1978). The Number 1 thiocarbamate pesticide is maneb, a fungicide, with 1974 estimated production of 5.4×10^3 metric tons (Archer *et al.*, 1978). Manzate is a combination of manganese and zinc forms of maneb/zineb. Oryzalin is a typical member of an important class of herbicides, the nitrated aromatics.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

TASK I - CARBON TREATMENT

1. Wastewater from manufacture of oryzalin can be treated by granular activated carbon. However, because of the high concentration of oryzalin and closely related compounds there is a large carbon requirement. In addition, the high concentration of ammonia (and possibly other non-colored components) is not sufficiently reduced to eliminate toxicity to fish. The ammonia also stimulates algal growth. Comparative studies with unformulated oryzalin suggest that the ammonia content, rather than the oryzalin content, is primarily responsible for fish toxicity. Ammonia could be removed by other processes, for example, air stripping at high pH. In practice, ammonia could be removed before or after carbon treatment for removal of the oryzalin and other colored compounds; or if sufficiently diluted with other wastewaters, could be biologically nitrified.

2. Currently recommended procedures for determining MSMA are based on arsenic measurement and do not distinguish between MSMA and its degradation products. Determination of MSMA itself can be performed by ion chromatography. MSMA is not appreciably removed from MSMA manufacturing wastewater by activated carbon treatment. The wastewater also contains substantial amounts of oxygen-demanding materials (including methanol) which are not significantly removed by activated carbon treatment.

3. Wastewaters from manufacture of atrazine and maneb contain large amounts of particulate pesticide. The liquid portion, therefore, is essentially a saturated solution. Economical carbon treatment

of these wastewaters, especially the atrazine wastewater, will require pretreatment for removal of these solids. Otherwise, the column will become clogged and the solid will also serve to saturate liquid passing through the column.

(4) Atrazine particulates are approximately 5-500 μm in diameter. After pretreatment by filtration, atrazine wastewaters are readily treated by activated carbon.

(5) In maneb manufacturing wastewaters the actual concentration of maneb is low, since the majority quickly degrades to the more stable compounds ethylene thiuram monosulfide (ETM) and ethylene thiourea (ETU). ETU has been implicated in causing adverse health effects in several species of animals. Maneb, ETM, ETU, and other maneb intermediates can be effectively removed by GAC treatment. An important finding was that breakthrough of ETU occurs well in advance of breakthrough of the other compounds. Therefore, in practice, monitoring of GAC performance should be directed toward ETU. Relatively quick and simple thin layer chromatography techniques could be adapted for routine ETU determinations.

(6) On the basis of its performance in adsorption isotherm studies, Calgon Filtrasorb 400 was employed for all pesticides in GAC column tests. Since virgin carbon was used, it cannot be assumed that this carbon would be best in long-term performance. Losses caused in regeneration may vary from carbon to carbon.

(7) While wastewaters from manufacture of atrazine, maneb, and oryzalin are all treatable by GAC, the large carbon requirements indicate that the cost of such treatment may be unattractive. Therefore, other methods of treatment should be investigated. In the meantime, it is reassuring to find that this widely used and accepted treatment method is effective.

TASK 2 - BIOLOGICAL TREATMENT

(1) Wastewater from oryzalin manufacture could not be treated biologically in 1:10 or 1:100 dilution in municipal sewage. The activated sludge units progressively lost sludge solids, and the color of the wastewater was not significantly reduced. It was noted, however, that some COD reductions were achieved. Additional testing indicated this to be due to simple aeration. Evidently some organic constituent of the wastewater is removed by air stripping. This component should be identified and the feasibility of treating (or pretreating before biological or GAC treatment) the oryzalin wastewater by this method should be investigated in further studies.

(2) In 1:10 dilution with municipal sewage, wastewater from atrazine manufacture did not interfere with operation of AS units under the conditions tested. On the other hand, atrazine was not significantly removed in the process. Part of the problem appeared to be due to transport of the fine atrazine particulates through the system, resulting in saturated liquid phases (~33 mg/l). GAC treatment was more effective in treating this wastewater.

(3) Activated sludge treatment of MSMA wastewater failed to satisfactorily remove either the pesticide or the arsenic from the wastewater. Some arsenic also tended to accumulate in the sludge, possibly portending failure of the AS system during longer runs (as would be encountered in actual practice). The methanol component is readily removed in AS treatment. It is suggested that other treatment processes, possibly coagulation/precipitation, be investigated for removal of arsenic prior to biological treatment.

(4) Effluents from AS units treating maneb wastewaters (1:10 in municipal sewage) contained substantial amounts of ETU, as well as oxygen-demanding materials. Therefore, under the conditions tested, biological treatment did not appear to be suitable for treating these wastewaters, whereas GAC treatment readily removed

ETU and other maneb decomposition products. Because of the presence of ETU in biological effluents at some concentrations of maneb wastewater, further studies should be conducted of effluents from maneb production diluted in various proportions with municipal wastewater in order to determine acceptable levels of maneb wastewater in municipal sewage.

SECTION 3

EXPERIMENTAL DESIGN, MATERIALS, AND METHODS

INTRODUCTION

As noted in Section 1, objectives of the tasks were to evaluate biological treatment and granular activated carbon treatment of selected actual pesticides manufacturing wastewaters. Biological treatability was evaluated in terms of bench scale activated sludge systems to (1) successfully operate on a mixture of municipal wastewaters and pesticide wastewaters and (2) remove the pesticide and other toxic materials in the wastewaters. Performance of granular activated carbon column treatment was evaluated by (1) analysis of pesticide and related compounds before and after treatment and (2) bioscreening of the influent and effluent of the columns.

Peltier and Tebo (1978) have pointed out that present EPA regulatory programs directed to the control of toxic wastewaters emphasize specific limits on individual chemicals, and they note that this approach has numerous shortcomings:

(1) there is little or no information on toxicity of thousands of chemicals in common use

(2) in many cases analytical methodology is unavailable or prohibitively expensive

(3) toxicity may be due to chemicals other than those for which the investigator has analyzed

(4) especially in wastewater discharges, the toxicity may be a function of the mixture of the chemicals.

Bioassays alone, however, may fail to identify causes of toxicity or suggest approaches to its control (Duke _et_ _al_., 1977). Miller _et_ _al_. (1978) reiterate these concerns stating that:

> "The continued acceptance of chemical analysis of specific constituents . . . as the primary reference standard for the legislation of ecological response criteria is both unwise and misleading. Only concurrent evaluations of both chemical analyses and bioassays results will provide the scientific base necessary to establish realistic water quality criteria."

For these reasons EPA-IERL has developed an integrated physical, chemical and biological approach, designated "Level 1 testing," for assessment of industrial effluents (Hamersma et al., 1976; Duke et al., 1977). An abbreviated version of this approach was utilized in assessing the treated and untreated pesticides manufacturing wastewaters investigated in these tasks. The tests, summarized below and detailed in the appendices, included the following:

(1) Routine wastewater characterization

(2) Analysis for specific pesticides

(3) Bioassays with freshwater fish and algae.

In conjunction with biological treatability studies, tests were also performed to evaluate toxicity of the wastewaters to domestic sewage and activated sludge microorganisms.

SAMPLING AND COLLECTION

In each case the manufacturer was asked to supply a 4-5 gallon grab sample of wastewater to be used in preliminary and screening studies. The atrazine wastewater was shipped by the manufacturer in a plastic carboy. In the other cases, RTI supplied the manufacturers with specially cleaned 1-gallon glass jugs with Teflon-lined caps, and requested that the samples be chilled after collection, then shipped in a special insulated container to RTI. Screening samples are designated Sample 1 in text below.

Large samples (30-60 gal) of wastewater were obtained by RTI personnel on site. The type of sample (grab or composite) was determined by the nature of the manufacturing process (batch or continuous). These samples were collected in 55-gallon drums lined with Teflon bags, or in 5-gallon glass jars with Teflon or aluminum foil lined caps. The samples were transported to RTI by RTI personnel and were kept chilled in transit. The samples were stored until analysis and testing in iced containers or under refrigeration. Large samples are designated Sample 2 in text below.

ANALYTICAL PROCEDURES

Routine Wastewater Characterization

Unless otherwise noted, wastewater analyses were conducted according to Standard Methods for the Examination of Water and Wastewater, 14th edition (APHA, AWWA, WPCF, 1976). The specific procedures used are shown in Appendix A. Routine analyses were conducted for pH, chloride, acidity, alkalinity, nitrogen forms, phosphorus, chemical oxygen demand (COD), and residues.

While the pH of natural waters is generally in the range of 4-9, industrial wastewaters, including those from pesticide manufacture, may be strongly acidic or basic. Extreme pH values may have diverse deleterious effects on both biotic and abiotic components of receiving streams or wastewater treatment plants. Such effects may include killing or inhibition of biological treatment system biota, toxicity to fish and other organisms, and corrosion.

High chloride levels are often associated with industrial wastewaters. Undesirable effects of high chloride concentration include toxicity to fish and other biota, interference with biological treatment systems, increased corrosion rate, and interference with certain physical-chemical wastewater treatment processes. The interference of chloride in analytical procedures for other wastewater parameters, for example the COD analysis, necessitates its early determination in wastewater samples.

Acidity, a measure of the capacity of a wastewater to neutralize a strong base, indicates the amount of base required to neutralize the wastewater to some desired pH. Acids in water affect corrosiveness, may interfere with biological processes, and influence solubility of other components. Alkalinity is the corresponding measure of the capacity of a wastewater to neutralize a strong acid.

Nitrogen may occur in industrial wastewaters in a multitude of forms. Ammonia is a common raw material in organic syntheses. In wastewaters it may (1) either stimulate or depress algal growth, depending on its concentration, (2) be toxic to fish and other fauna, (3) exert an oxygen demand due to its potential for being nitrified.

Nitrate and nitrite, the oxidized forms of nitrogen, serve as plant nutrients. They are typically found in effluents from biological nitrification systems. Numerous compounds may be responsible for the organic nitrogen content of wastewaters. Such compounds are frequently encountered in effluents from manufacture of synthetic organic pesticides. A gross measure of the combined organic and ammonia-nitrogen content of wastewaters is given by the total Kjeldahl nitrogen analysis.

Phosphorus generally occurs in wastewaters in the form of organic or inorganic phosphates. It is required for growth of all organisms, and since it is frequently the limiting factor in productivity of freshwaters, its presence in effluents may contribute to undesirable stimulation of algal growth.

In reference to nitrogen and phosphorus, it should be noted that the organisms responsible for biological wastewater treatment, like all organisms, require these nutrients. Some industrial wastewaters are deficient in nitrogen and phosphorus in proportion to the amount of organic carbon present, and in such cases successful biological treatment may require addition of N and P.

The COD determination is a measure of the amount of oxygen which would be required to chemically oxidize organic matter. It is, therefore, indirectly an estimate of the organic content of a sample. With wastes containing toxic substances, this test or a total organic carbon determination is especially useful in determining the organic load since the biochemical oxygen demand (BOD) test may be subject to inhibition.

Residue determinations indicate the amount of dissolved or suspended solids in a wastewater. They are useful in determining the utility of various solids separation procedures, such as settling or filtration, in treating the wastewater, as well as estimating the amount of sludges which will be produced. High dissolved solids levels may be indicative of the presence of salts, such as chlorides, which may have adverse effects. A high dissolved solids level in itself will affect the osmotic pressure of the solution and thus affect biological activity.

Wastewaters from manufacture of organoarsenical pesticides, such as MSMA, contain arsenic. Arsenic may be acutely toxic to organisms or it may produce chronic toxic effects as it accumulates over time. Arsenic determinations were conducted by an atomic absorption procedure, as described in Appendix B.

Pesticide Analyses

As noted above, major criteria for effectiveness of the wastewater treatment processes were (1) ability to reduce or eliminate toxicity and (2) ability to reduce or eliminate the pesticide component. In accordance with the second criterion, it was necessary to find or to develop procedures for determining concentration of the specific pesticides in a wastewater matrix containing a multitude of organic compounds, including such closely related compounds as raw materials and breakdown products. This proved to be a major challenge in conducting the project since in several cases adequate methods were not available.

Atrazine--

Atrazine was analyzed by gas chromatography by a procedure adapted from Richard *et al*. (1975). The procedure is detailed in Appendix C.

Oryzalin--

Oryzalin in pure solutions can be measured by ultraviolet-visible (uv-vis) spectroscopy. The wastewaters from oryzalin manufacture, however, contained other colored components. Presence of these components was confirmed by uv-vis spectroscopy and by thin-layer chromatography. Oryzalin in wastewaters was determined by gas chromatography/electron capture detection (GC/ECD) by the method of Sieck *et al*. (1976). The procedures are described in Appendix D.

MSMA - Monosodium Methanearsonic Acid

None of the currently available analytical methods were adequate for determining MSMA in a mixture containing other arsenic compounds. Since the raw manufacturing wastewater and the effluents from the pilot activated sludge units contained arsenic in several forms, it was necessary to develop a method for specific determination of MSMA. Preliminary experiments with a new technique, ion chromatography (Small, et al., 1975), indicated that methyl arsonic acid and arsonic acid could be distinguished and quantitated by selection of appropriate columns. MSMA in the raw manufacturing wastewaters and the effluents from activated carbon treatment was readily determined. In combination with domestic wastewater, as in the influents and effluents of the activated sludge units, chloride interfered with the MSMA analysis. It was necessary to develop a preparative procedure to remove chloride prior to ion chromatographic analysis. The detailed procedures for analysis of MSMA in wastewater are given in Appendix E. Insofar as is known, they represent the first methods for specifically determining MSMA in the presence of related arsenic compounds.

Maneb and its Breakdown Products--

Maneb occurs in wastewaters in combination with its breakdown products, ethylene dithiocarbamate disulfide (ETD) or monosulfide (ETM) and ethylene thiourea (ETU). Maneb was determined by a procedure adapted from McLeod and McCully (1969) involving its reduction to carbon disulfide, which is then measured by GC/ECD. Breakdown products were determined by thin layer chromatography (Czeglédi-Jankó, 1967) followed by scanning spectrodensitometry. Details are given in Appendix F.

TREATABILITY TESTS

Activated Carbon Tests

As indicated in Section 7 (below), there is a considerable body of data indicating the ability of activated carbon to adsorb pesticides and other organic materials from solution. However, most of the extant data deal with sorption of pesticides from (1) dilute solutions prepared from analytical grade compounds, (2) potable water sources, or (3) agricultural runoff. Relatively little information has been published on performance of activated carbon for treatment of actual pesticide manufacturing wastewaters. For protection of proprietary information on pesticide processes, the published data generally do not disclose characterization of the wastewater components and in only a few instances have both biological and chemical assessment been attempted. Sontheimer (1976) and others have stressed the need for realistic laboratory tests for evaluating activated carbon, noting that tests should be conducted on samples representing the concentration ranges and mixtures of chemicals present in the wastewater to be treated. In this task, actual pesticide wastewaters were employed, and the treated and untreated wastewaters were subjected to both biological and chemical assessment.

For preliminary assessment of ability of various carbons to remove pesticide from the wastewaters, liquid adsorption isotherm tests were conducted using a procedure adapted from Metcalf and Eddy, Inc. (1972) (Appendix 7). Based on its performance in liquid isotherm tests, Calgon Filtrasorb 400 was selected for large-scale tests with granular activated carbon (GAC) columns (Appendix 7). Influent and effluents were analyzed for COD and pesticide content. Toxicity tests with fish and algae were conducted on the untreated (influent) and treated (effluent, first fraction) wastewater.

Activated Sludge Tests

Biological treatment is often the most cost-effective method of removing organic matter from municipal and industrial wastewaters. Such treatment relies on the ability of mixed cultures of microorganisms to remove organic pollutants by sorption, degradation to innocuous end products or incorporation into new growth. Since biological treatment systems rely on living organisms, it is necessary (1) that the organics to be removed be biodegradable and (2) that the wastewaters do not contain toxic materials in concentrations which inhibit biological activity. Fortunately, due to the variety and adaptability of microorganisms, it is often possible to adapt or acclimate biological treatment systems to tolerate and to treat toxic and/or refractory materials.

One of the most commonly employed biological treatment systems utilizes the activated sludge process. In this process high concentrations of microorganisms (activated sludge) are maintained in suspension (mixed liquor) with oxygen and mixing supplied by forced aeration. With appropriate control of oxygen levels, pH, quantity and quality of feed (wastewater) and exposure period (detention or retention time), activated sludge organisms are capable of rapid removal of organics and their accompanying oxygen demand.

In practice the activated sludge process generally operates on a continuous feed basis. Fortuitously, it is possible to simulate the process on a greatly reduced scale so that biological treatability of wastewaters can be evaluated in the laboratory. For the studies conducted in this project, the miniature complete mix continuous activated sludge unit designed by Swisher (1970) was employed. To simulate effect of discharge of pesticide manufacturing wastewaters to publicly owned treatment works, the units were fed a mixture of the pesticide wastewater and domestic sewage. Treatability of a wastewater mixture was evaluated in terms of (1) its effect on operation of the units and (2) the ability of the units to remove the pesticide and to produce an effluent in which toxicity was reduced or eliminated. Details of the system are given in Appendix H.

ECOLOGICAL ASSESSMENT TESTS

The reasons for including ecological tests in assessment of industrial wastewater treatability were outlined above. Due to time, space, and financial constraints, it was not possible to conduct complete ecological assessment testing on the wastewaters. Two tests, the static fish bioassay and the algal assay procedure bottle test, were chosen on the basis of their established value in predicting effects of toxicants on freshwater biota. These level 1 tests (Duke *et al*., 1977) are also included in *Standard Methods for the Examination of Water and Wastewater* (APHA *et al*., 1976). The fish assay is the oldest standard method for assessing toxicity of wastewaters. The relatively new algal assay procedure employs the green alga *Selenastrum capricornutum* and may be used to detect stimulatory, inhibitory, or toxic effects. Miller *et al*. (1978) reviewed studies of 23 textile wastewaters using 7 of the tests and concluded that the algal assay test was the most sensitive and had the additional advantage in that it not only identified toxic wastes but also those that were stimulatory. In regard to pesticide wastewaters, it is noteworthy that green algae are often very sensitive to herbicides, especially those herbicides which act by inhibiting photosynthesis, and consequently green algae are frequently employed in bioassays of herbicide residues (Greaves *et al*., 1976).

The algal assay procedure is described in detail in Appendix I; the fish bioassay procedure, in Appendix J.

TEST OF EFFECTS OF PESTICIDE WASTEWATERS ON DOMESTIC SEWAGE AND ACTIVATED SLUDGE ORGANISMS

Biological treatment systems rely on activity of the diverse community of bacteria, fungi, protozoa, and other organisms which are able to utilize for food and energy the organic constituents of the wastewater. In municipal wastewater treatment systems domestic sewage influent is both a source of organisms and of readily available organic compounds. In the biological treatment units many additional species of adventitious organisms develop. Industrial wastewaters, however, often contain constituents which are inhibitory or toxic to organisms, especially if the biological treatment system has not been acclimated to these constituents.

Potential adverse effects of industrial wastewaters on biological treatment systems can often be predicted in relatively simple and inexpensive tests in which the organisms are exposed to a mixture of domestic sewage and the industrial wastewaters.

One such test is a modification of the agar diffusion method used in assaying sensitivity of bacteria to antibiotics (Brock and Brock, 1973). Basically, a petri plate containing an agar medium is prepared and evenly inoculated with the test organism. Then, a filter paper disc containing a measured amount of the test substance is placed on the surface of the agar. During incubation (generally 24-48 hr) the test substance diffuses some distance into the agar, and if the test organism is sensitive to the substance, no growth occurs in the area adjacent to the disc. After incubation, inhibitory effects are readily apparent as clear zones of no growth adjacent to the disc, surrounded by heavy growth in areas where the test substance is absent or present in a lower concentration.

For these tests, petri plates were prepared from nutrient agar (Difco) containing 1.5% agar. The surface of each plate was evenly spread with 0.5 ml of raw domestic sewage. The plate was allowed to stand for an hour to permit the sewage to soak into the agar. Then, a sterile filter paper disc was placed in the center of the plate and dosed with 0.1 ml of the pesticide wastewater (or a dilution thereof). The plates were incubated at 25°C for 48 hr and observed for zones of inhibition around the disc.

A test which can be used to detect toxicity of wastewater components to activated sludge is the oxygen consumption rate test (Method 213B, APHA et al., 1976). In the presence of suitable food sources and the absence of toxic materials healthy activated sludge consumes oxygen at a steady rate proportional to the amount of food present. In the presence of toxic materials, this rate is decreased, and oxygen consumption may cease altogether in cases of severe toxicity. By adding various percentages of an industrial wastewater to the feed to activated sludge and measuring rate of oxygen consumption under each condition, it is possible to estimate whether or not the wastewater is toxic, and if so, at what dilution it can be tolerated by the sludge. In full-scale treatment plants such testing is used in detecting at an early stage potential problems in activated sludge operation, problems which could possibly be controlled by eliminating entrance of a toxic stream into the system or by reducing the proportion of that stream in the influent to a level tolerable by the system. In studies conducted in this project, the oxygen consumption rate test was performed to see how well the results correlated with those obtained in the more extensive activated sludge treatability tests. Tests were conducted as described in Method 213B (APHA et al., 1976), using activated sludge from a municipal wastewater treatment plant (Hope Valley Plant, Durham, NC). The test container was a BOD bottle, and oxygen consumption and temperature were monitored with a polarographic oxygen sensitive membrane electrode equipped with a self-stirring device (Yellow Springs Instrument Company).

SECTION 4

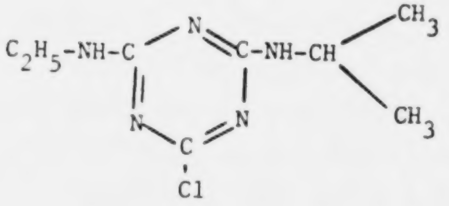
ATRAZINE WASTEWATER TREATABILITY STUDIES

GENERAL BACKGROUND INFORMATION

Pesticide: Atrazine CAS No. 1912-24-9

Gesaprim^{TM}; Aatrex^{TM}; Atrasol^{TM}; G-30027

Structure



2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine

Chemical Category

Triazine; other triazines include simazine, propazine, cyprozine, terbuthylazine, cyanazine, prometone, secbumetone, terbumetone, desmetryn, ametryn, prometryn, metoprotryn, terbutryn, aziprotryn, dimethametryn, dipropetryn.

Properties

Colorless crystals, m.p. 173-175 C; v.p. 3.0×10^{-7} mm Hg at 20 C. (Martin and Worthing, 1974). pKa (21 C) = 1.7; density of 1.187 g/cm^3 (Esser *et al*., 1975). Soluble in 2% alcohol. Solubility in water at 20-25 C is 33 mg/l (Esser *et al*., 1975), with the atrazine dissolving according to a first order reaction, the solubility and rate constant increasing with temperature (Calvet *et al*., 1975). The activation energy of solubilization is approximately 4.1 - 4.8 kcal/mole, i.e., there is a 30% decrease in time required for 50% solubilization when the temperature increases by 10 C (Calvet et al., 1975). Sol. in methanol, 18,000 mg/l; in chloroform, 52,000 mg/l (Martin and Worthing, 1974). Stable in neutral, slightly acidic, or basic media, but hydrolyzed to the herbicidally inactive hydroxy derivative by alkali or mineral acids at higher temperatures; non-corrosive (Martin and Worthing, 1974). Undergoes photodecomposition with ultraviolet light in aqueous solution to form the 2-hydroxy analogs (Esser et al., 1975); acetone may serve as a photosensitizer (Burkhard and Guth, 1976).

Intended Use

Herbicide. Registered in 1958 as a herbicide. Used as selective pre- and post-emergence herbicide on numerous crops, including corn, sorghum, sugar cane, and nursery conifers (Martin and Worthing, 1974). Recommended for use in fish ponds for selective control of farm pond weeds, especially submerged aquatics (Johnson, 1965).

Mode of Action

Taken up by roots or foliage; inhibits growth of most plant organs; at subtoxic levels may increase chlorophyll content, and resistant crops may be a darker green; inhibits photosynthesis within photosystem II at the stage where water is photolysed; inhibits respiration; causes pollen cell abnormalities in pollen cells of grain sorghum, but has no effect on yield (Brian, 1976). Little if any effect on structure of chloroplast of the green alga *Chlorella ellipsoidea*, but causes degradation of chloroplasts of barnyard grass; does not affect mitochondria at up to 20 ppm; causes chromosomal aberrations in several plants (Linck, 1976). Inhibits photosynthetic CO_2 fixation but does not affect dark fixation of CO_2 in corn, cotton, and soybeans (Frans et al., 1972).

Manufacturing Information

Amount Produced Annually: 49.9×10^3 metric tons in 1974 (Archer et al., 1978)

Manufacturers	Locations
Ciba-Geigy	St. Gabriel, LA
Missouri Chemical Company	St. Joseph, MO
Vertac, Inc.	Vicksburg, MS

According to a recent farm periodical, "Big Farmer" (Anon. 1977), other companies either make or formulate atrazine products since atrazine products are listed as being available from Monsanto, Dow, Stauffer, Drexel, and Shell companies.

Atrazine has the largest use volume of any pesticide in the United States.

Health and Ecological Effects

Toxicity--

Oral, LD_{50}, rat, 2000 mg/kg (Weber, 1977); 3080 mg/kg (Martin and Worthing, 1974).

Mouse, 1750 mg/kg (Martin and Worthing, 1974).

Acute dermal LD_{50}, rabbit, 7500 mg/kg (Martin and Worthing, 1974).

Not tumorigenic to the mouse at 10-22 mg/kg/day (Hayes, 1975).

LD_{50}, fish, 12.6 mg/l (Weber, 1977).

Toxic to the carp Cyprinus corpio L. at 35 mg/l and to the trout Salmo irideus at 5-30 mg/l (Lüdemann and Kayser, 1965)

Toxic at levels as low as 3 ppm to fry of the fish Coregonus fera (Gunkel and Kausch, 1976).

Toxic to daphnia at approximately 20 mg/l (< 50% killed) (Lüdemann and Kayser, 1965).

With Daphnia magna and Moina rectirostris, at 1 ppm over 30-45 days increases duration of embryonic and postembryonic development, as well as decreases number of broods and number of offspring per brood. (Shcherban, 1973).

Limiting value for tubifex worm, 300 mg/l (Lüdemann and Kayser, 1965).

Atrazine at nontoxic levels acts synergistically with certain insecticides, such as carbofuran, DDT, parathion, and diazinon, to significantly enhance their toxicity to the fruit fly (Lichtenstein et al., 1973).

Fate in Soils--

Half-life in soil, 26-78 weeks (Weber, 1977); may be adsorbed by components such as montmorillonite (Calvet and Tercé, 1975).

Effect on nitrification in the soil is unresolved, as both stimulatory and inhibitory effects have been noted (Greaves *et al*., 1976).

Atrazine treatment of soils does not affect subsequent crops of sensitive species if residuals are <0.13 mg/l (Fusi and Franci, 1972).

Atrazine at 10^{-3} concentration produced no evidence of mutagenic influence on the haploid flowering plant *Pelargonium* (Pohlheim *et al*., 1977).

Monitoring of several major U. S. rivers and tributaries indicated that atrazine is detectable year round, at values generally less than 1 ppb; no nitrosoatrazine was found in the samples (Newby and Tweedy, 1976).

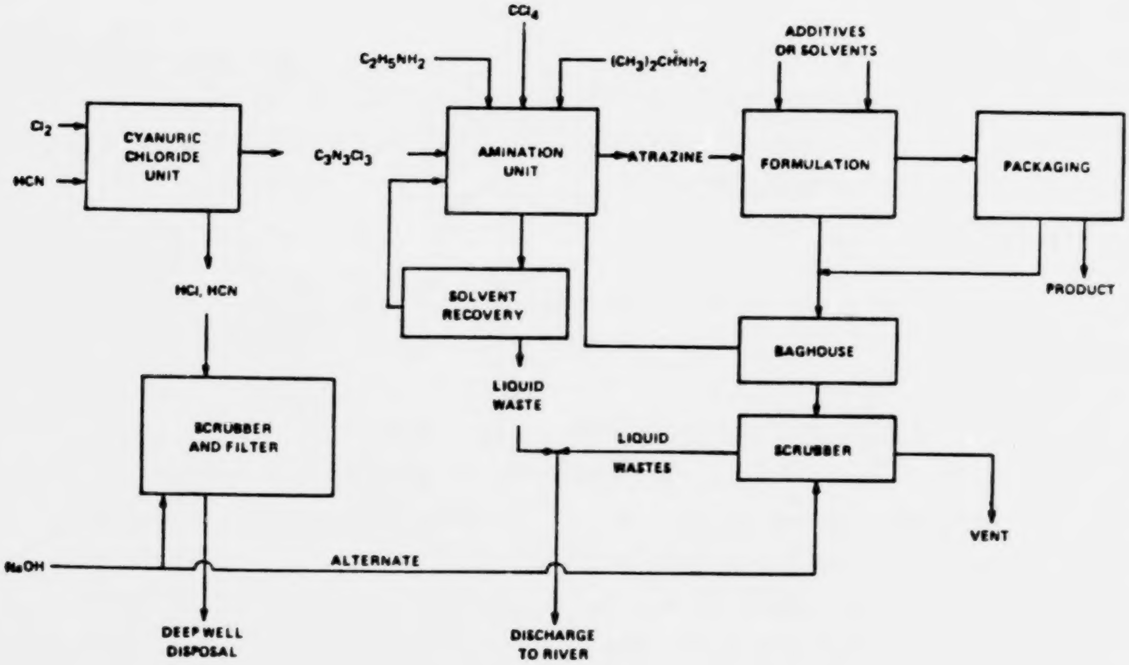
Mutagenic Potential--

Atrazine alone produces no mutagenic effects in the usual short-term tests for mutagenicity. For example, there is no effect on *Tradescantia* hair cells and no evidence of cytogenetic activity on root tips of *Hordeum*, *Vicia*, and *Sorghum vulgare* (Müller *et al*., 1972). At 10^{-3} M concentration, it produces no evidence of mutagenicity in the haploid flowering plant *Pelargonium* (Polheim *et al*., 1977). However, it does induce genetic alterations in maize germ cells (Plewa and Gentile, 1976) and extracts from atrazine-treated maize do show mutagenic activity (Gentile and Plewa, 1976). Extracts from maize kernels treated with 5 and 20 ppm increased mitotic gene conversion in the yeast *Saccharomyces cerevisiae* by (respectively) 2.5 and 4 times over controls, whereas a 100 mg/l solution of atrazine alone had no effect; even greater activity was found in leaf extracts (18-30 times over controls) leading to speculation as to the food chain effect (Gentile and Plewa, 1976).

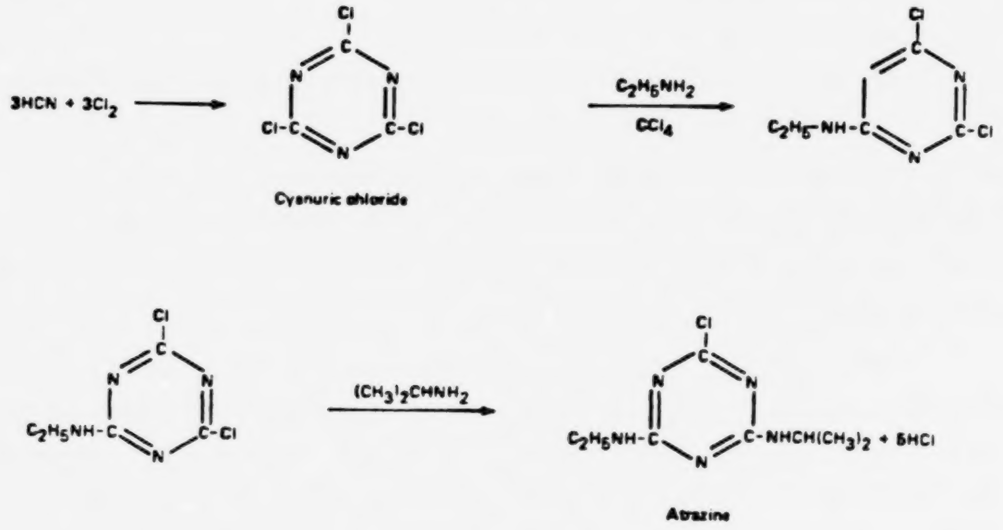
Manufacturing Process

Atrazine may be prepared by reaction of cyanuric chloride with one equivalent of ethylamine followed by one equivalent of isopropyl amine in the presence of an acid-binding agent (Sittig, 1977). The charts shown below represent idealized schemes. They do not necessarily represent individual plants, which vary somewhat in production processes.

(1) General production and waste scheme for atrazine (Sittig, 1977).


CCl_4
$C_2H_5NH_2$
$(CH_3)_2CHNH_2$
ADDITIVES OR SOLVENTS
Cl_2
HCN
CYANURIC CHLORIDE UNIT
$C_3N_3Cl_3$
AMINATION UNIT
ATRAZINE
FORMULATION
PACKAGING
HCl, HCN
SOLVENT RECOVERY
PRODUCT
BAGHOUSE
LIQUID WASTE
SCRUBBER AND FILTER
LIQUID WASTES
SCRUBBER
VENT
NaOH
ALTERNATE
DEEP WELL DISPOSAL
DISCHARGE TO RIVER

(2) General chemistry of atrazine production (Sittig, 1977).


3HCN + 3Cl2
Cyanuric chloride
C2H5NH2
CCl4
C2H5-NH-C
C-Cl
(CH3)2CHNH2
C2H5NH-C
C-NHCH(CH3)2 + 5HCl
Atrazine

Current Waste Disposal Practice

Atrazine manufacturing wastewater may be treated by activated carbon or by chemical hydrolysis.

As noted above, atrazine may be hydrolyzed to the inactive hydroxy form under either acid or alkaline conditions, the rate being strongly dependent on temperature and pH. Shih and Dal Porto (1975) indicate the half-life under various conditions as follows:

pH	Temperature, °C	Half-life
1	25	80 hr
1	80	4.7 hr
3	25	331 hr
12	25	295 hr
14	25	4.5 hr
16	80	16 min

They summarize a recommended detoxification scheme for triazine wastewater as follows:

(1) adjust pH to 1 or to 14

(2) pass through a hot water heater

(3) discharge to a holding pond

(4) monitor herbicide concentration to determine when effluent may be discharged.

An alternate treatment scheme, using granular activated carbon, is employed by at least one manufacturer. The treatment includes sand filtration, passage through Calgon Filtrasorb carbon and neutralization, as shown in Figure 1.

Lawless et al. (1972) described the disposal of wastes at Ciba-Geigy, St. Gabriel, LA. Liquid effluents from the cyanuric chloride unit were subjected to pH adjustment and filtration prior to deep well disposal (6000 ft deep), and the remainder of the liquid wastes were discharged to a river, contributing 500 lb of BOD/day at the 100 million pound per year production rate. Lawless et al. noted that the wastes contained large amounts of NaCl.

CHARACTERIZATION OF WASTEWATER FROM ATRAZINE MANUFACTURE

At the plant of the manufacturer sampled, the wastewater stream of interest was easily segregated. The manufacturer shipped the first small sample to RTI. The large sample was collected and composited by RTI personnel at the plant site.

The atrazine product occurs as fine solids, some of which escape into the waste stream. The final unit process is continuous and is in operation year-round. The wastewater flow from atrazine manufacture averages 144,000 gpd (range of 100,000-200,000 gpd). The atrazine concentration shows substantial fluctuation, depending on plant operating conditions. This is largely due to variations in the amount of fine solids escaping. The company currently filters the wastewater through sand filters, then through two GAC columns (Calgon Filtrasorb) in series, before discharge to a municipal treatment plant. The company states that removal of pesticide averages >99%, but notes that escape of solids at times results in higher effluent

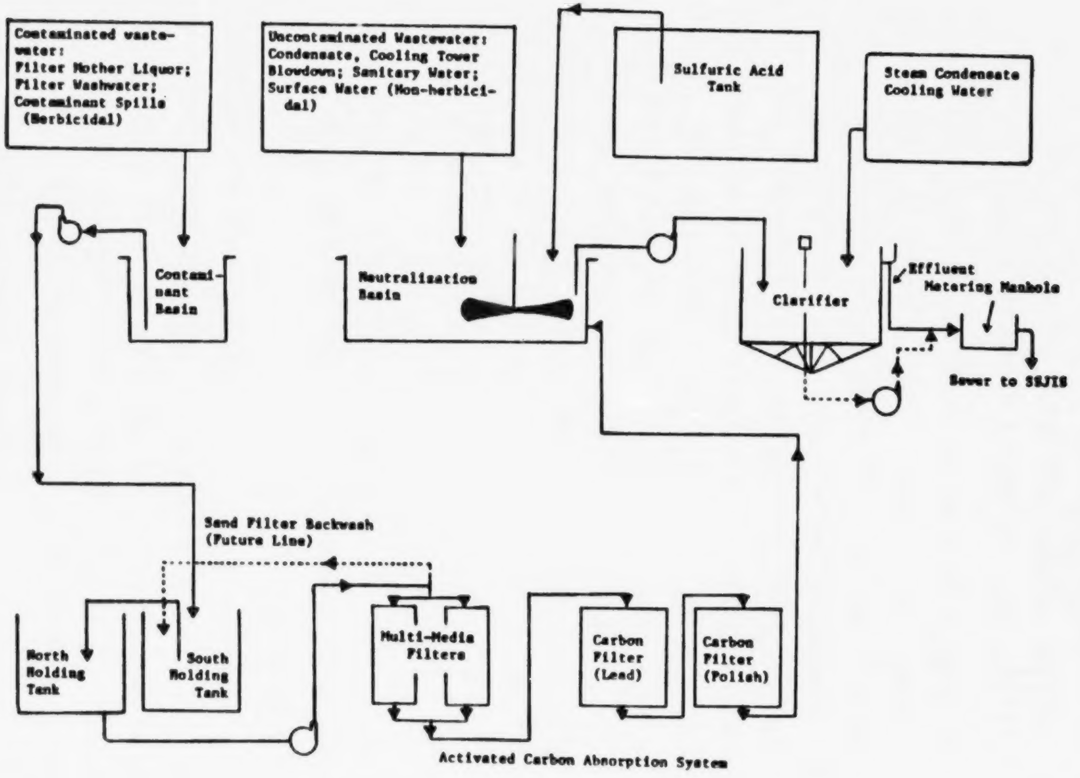

Contaminated waste-water:
Filter Mother Liquor;
Filter Washwater;
Contaminant Spills (Herbicidal)
Uncontaminated Wastewater:
Condensate, Cooling Tower Blowdown; Sanitary Water;
Surface Water (Non-herbicidal)
Sulfuric Acid Tank
Steam Condensate Cooling Water
Contaminant Basin
Neutralization Basin
Clarifier
Effluent
Metering Manhole
Sewer to SSJTS
Send Filter Backwash (Future Line)
North Holding Tank
South Holding Tank
Multi-Media Filters
Carbon Filter (Lead)
Carbon Filter (Polish)
Activated Carbon Absorption System

Figure 1. Schematic diagram of treatment of atrazine manufacturing wastewater.

concentrations. (In further studies the possibility of more efficient solids capture by coagulation and flocculation processes should be investigated).

As shown in Table 1, the samples obtained by RTI were nearly neutral in pH. In addition to the pesticide content, other parameters of interest include the high chloride and Kjeldahl nitrogen content, the high soluble COD and dissolved solids, and the highly variable settleable solids.

The wastewater samples from the atrazine manufacturer sampled contained a variable amount of suspended solids. These samples of wastewater represented the influent into the carbon treatment system at the plant. To determine the contribution of these solids to the pesticide content of the wastewater, atrazine was determined in the total wastewater and in the solids and liquid portions after centrifugation for five minutes (International Clinical Centrifuge, Model CL, speed setting No. 3). Results are shown in Table 2. These results indicate that the majority of the atrazine is in the solids portion and that treatment to effectively remove these solids would reduce the load of pesticide to be removed in activated carbon or biological treatment. They also indicate that all of the solids were not removed by centrifugation since the atrazine concentration exceeds the solubility in water (33 mg/l).

An examination of the solids with the aid of a microscope indicated them to be long slender crystalline rods, 5-50 μm long. The rods occurred singly, rather than in clumps.

Fish toxicity screening tests were conducted with the wastewater. These indicated the LC_{50} to be > 10 ml/l (1%). Further screening tests were conducted on the liquid phase and the solid phase after centrifugation. The solid phase was reconstituted to the original wastewater volume in glass-distilled deionized water. Results are shown in Table 3.

These results indicated that the solid phase equilibrated with the liquid phase and that the resulting solution was equally as toxic as the total wastewater. They also provided evidence that LC_{50} for the wastewater was between 10 and 100 ml/l (1 and 10%).

Table 1. CHARACTERIZATION OF ATRAZINE WASTEWATER

Parameter	Sample 1	Sample 2
pH	7.0	7.8
Cl^-, mg/l	7,100	10,200
Alkalinity, mg/l as $CaCO_3$	375	465
TKN, mg/l	137	630
NH_4-N, mg/l	81	49
NO_2-N+NO_3-N, mg/l		2.0
TP, mg/l		0.3
COD, mg/l	4,466	2,100
Sol. COD, mg/l		1,800
Suspended solids, mg/l		390
Total solids, mg/l	17,500	10,050
Total dissolved solids, mg/l		9,660
Settleable solids, ml/l	62	1.0
Atrazine, sol., mg/l	87	37.4

Table 2. ATRAZINE CONTENT OF LIQUID AND SOLIDS PORTIONS OF ATRAZINE MANUFACTURING WASTEWATER

Sample		Atrazine, mg/l
Replicate 1 -	Liquid portion	94.1
	Solids portion	1850.0
Replicate 2 -	Liquid portion	70.0
	Solids portion	1880.0

Table 3. TOXICITY TO FISH OF SOLID AND LIQUID PHASES OF ATRAZINE MANUFACTURING WASTEWATERS

Sample	Wastewater Concentration ml/l	Wastewater Concentration %, v/v	Replicate	No. Fish Surviving at 96 hr (Initial=3)
Control	0	0	1	3
	0	0	2	3
Liquid Phase	10	1	1	2
			2	3
	100	10	1	0
			2	0
Solid Phase	10	1	1	2
			2	3
	100	10	1	0
			2	0

Full scale fish toxicity tests (Appendix K) showed the 96 hr LC_{50} to be 18 ml/l (1.8%) for both filtered and unfiltered wastewater. This was surprising, in that (1) it was expected that dilutions of the unfiltered wastewater would be more toxic since they would contain sufficient solids to produce a saturated solution and (2) it was expected that the LC_{50} for the filtered wastewater would be more than 1.8% since this concentration would provide ~0.6 mg/l of atrazine, much lower than the reported LC_{50} to fish (3-35 mg/l). It is possible that components other than atrazine were partially responsible for the observed toxicity.

From a technology control standpoint, a raw wastewater with an LC50 of 18 ml/l (1.8%, v/v) would be expected to be toxic in 96 hr to approximately 50% of the fish in a receiving body even if diluted ~60 times. With an application factor of 0.1, 600 volumes of receiving water would be necessary per volume of raw wastewater.

The effect of filtered atrazine wastewater on algal growth was determined. Preliminary studies with the initial "grab" sample provided by the company showed that no growth occurred at wastewater concentrations of 1 and 10% (v/v) and that growth occurred at 0.1 and 0.01% after a ten-day lag period. Full-scale studies were conducted with the composited wastewater samples (Appendix K). Wastewater concentrations greater than 0.01% inhibited growth during the first 10 days of incubation, while at 0.01% the total growth achieved during incubation was less than half that of the control. At a wastewater concentration of 0.01%, the I_{14} was 60%. While this is not considered a drastic reduction in growth, it is noteworthy that concentrations of the wastewater as low as 0.01% consistently reduced algal growth. This is not surprising since green algae often respond to the herbicides effective against higher plants.

ACTIVATED CARBON TREATABILITY STUDIES

Adsorption Isotherm Studies

Adsorption isotherm studies were conducted with a variety of carbons (Table 4, Figure 2). The most effective carbon overall proved to be Calgon Filtrasorb 400, although the difference was not great. Adjustment of pH, from pH 7 to pH 6, did not improve the removal of atrazine. The value of

Table 4. LIQUID ADSORPTION ISOTHERM DATA FOR ATRAZINE WASTEWATER

Carbon	M Wt. of Carbon g/100 ml of solution	C Residual Pesticide, mg/1	X Pesticide Adsorbed, mg/1	X/M Pesticide Adsorbed, g/g	X/M at C_o
1. Union Carbide, LCL	0	42.2	0	0	
pulverized GAC	0.08	42.0	0.2	~0	
	0.16	42.2	0	0	
	2.00	6.7	35.5	0.0018	<0.01
	2.50	4.6	37.5	0.0015	
2. Nuchar S-A	0	39.6	0	0	
	0.04	31.6	8.0	0.02	0.02
	0.08	31.6	8.0	0.01	
	0.16	8.0	32.6	0.02	
	2.0	12.1	27.6	0.001	
3. Calgon Filtrasorb	0	34.4	-	-	
400, pH 7.0	0.04	22.6	11.8	0.03	
	0.08	6.7	27.7	0.04	
	0.16	0.4	34.0	0.02	
	2.0	0.0	34.4	0.002	
					0.04
4. Calgon Filtrasorb	0	31.6	-	-	
400, pH 7.0	0.04	23.1	8.5	0.02	
	0.08	14.8	16.8	0.02	
	0.16	1.5	30.1	0.02	
	2.0	0.0	31.6	0.001	
					0.02

(continued)

Table 4. (continued)

Carbon	M Wt. of Carbon g/100 ml of solution	C Residual Pesticide, mg/l	X Pesticide Adsorbed, mg/l	X/M Pesticide Adsorbed, g/g	X/M at C_o
5. Calgon Filtrasorb 400, pH 6.0	0	39.4	-	-	
	0.04	23.2	16.2	0.04	
	0.08	10.8	28.6	0.04	
	0.16	1.5	37.9	0.02	
	2.0	0.0	39.4	0.002	
					0.04
6. RX WV-G	0	31.6	-	-	
	0.04	22.8	8.8	0.02	
	0.08	17.2	14.2	0.02	
	0.16	2.6	29.0	0.02	
	2.0	0.0	31.6	0.002	
					0.02
7. RX WV-L	0	31.6	-	-	
	0.04	22.8	8.8	0.02	
	0.08	-	-	-	
	0.16	2.1	29.5	0.02	
	2.0	0.0	31.6	0.002	
					0.02
8. Nuchar WV-G, pulverized	0	29.7	-	-	
	0.04	24.5	5.2	0.01	
	0.08	18.7	11.0	0.01	
	0.16	12.9	16.8	0.01	
	2.0	0.2	29.5	0.002	
					0.02

(continued)

Table 4. (continued)

Carbon	M Wt. of Carbon g/100 ml of solution	C Residual Pesticide, mg/1	X Pesticide Adsorbed, mg/1	X/M Pesticide Adsorbed, g/g	X/M at C_0
9. Union Carbide LCL	0	29.7	-	-	
	0.04	29.5	0.2	0.005	
	0.08	-	-	-	
	0.16	28.3	1.4	0.009	<0.01
	2.0	0.3	29.4	0.002	
10. Nuchar WV-L,	0	29.7	-	-	
pulverized	0.04	26.6	3.1	0.008	
	0.08	25.1	3.1	0.004	
	0.16	14.0	15.7	0.010	<0.01
	2.0	0.2	29.5	0.02	
11. Union Carbide LCK	0	29.7	-	-	
	0.04	28.3	1.4	0.004	
	0.08	27.0	2.7	0.003	
	0.16	21.5	8.2	0.005	
	2.0	0.4	29.3	0.002	
					<0.01

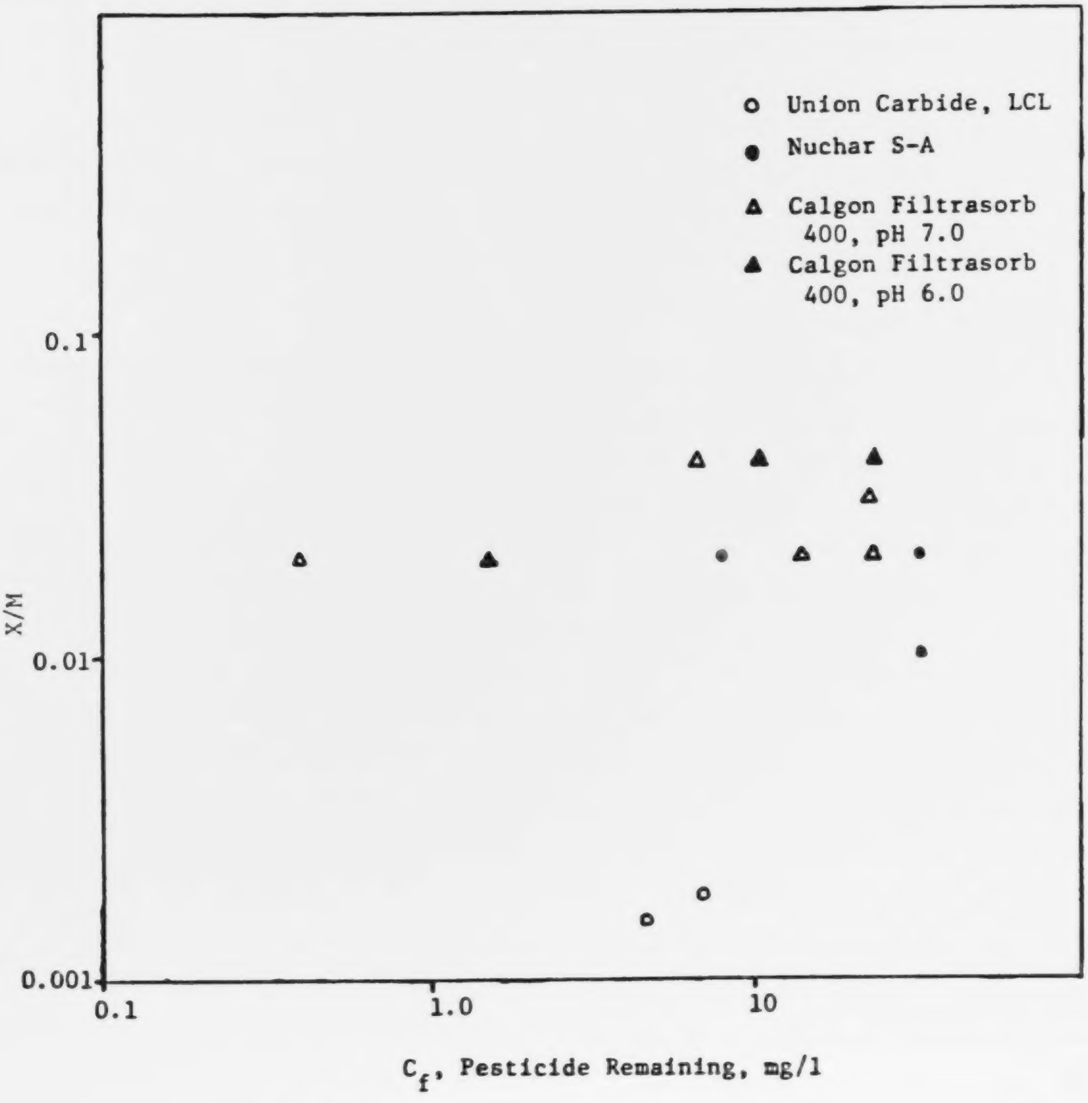


Figure 2. Adsorption isotherm of atrazine manufacturing wastewater.

X/M at C_0 is used as the measure of adsorptive capacity of carbons. Generally, carbon systems are considered economically feasible if this value is >0.10, questionable if between 0.05-0.10, and not feasible at values <0.05. The best value achieved in the adsorption test reported here was 0.04, therefore the utility of carbon could be considered to be marginal at best for this application.

Figure 2 shows a plot of some of the values obtained. The slight slope of the curves for each carbon tested indicates that there is comparable adsorption of the atrazine over a range of concentrations. This is borne out by the data in Table 4 (column X/M). Because activated carbon did remove atrazine to nondetectable levels, since carbon treatment is presently used at the plant tested, and because no better alternative treatments have been found, studies were continued with GAC columns.

GAC Column Studies

Column studies were initially conducted in a long column, but it soon became apparent that a very large volume of wastewater would be required to achieve breakthrough. The test was repeated in a smaller column which was 2.2 cm (i.d.) and contained 26.6 g of carbon. Bed volume was 57.9 ml, and the flow rate was 10 ml/min (0.64 gpm/ft^2). In this column breakthrough to the ppm level occurred after 67.2 bed volumes (Table 5, Figure 3). Before breakthrough the atrazine was removed to ppb levels and the COD was reduced by approximately 65%. Simple filtration of the wastewater before carbon treatment also achieved some COD reduction (Table 5). It should be noted that the remaining COD is still 2-3 times that of raw domestic sewage and may require additional treatment for removal. Assuming that breakthrough occurs at 67 bed-volumes, carbon requirements for the wastewater will be 6.85 g/L (67 lb/1000 gal).

In studies conducted by Calgon Corporation on 20 wastewaters from industrial organic chemicals production, carbon requirements for TOC removal ranged from 0.4-1496 lb/1000 gal, with the majority falling between 10-200 lb/1000 gal (Hager, 1974). Hager noted that "carbon exhaustion rates are clearly in excess of those associated with domestic sewage treatment" and that treatment costs for industrial wastewaters fall in the $/1000 gal treated, compared to 10-30¢/1000 gal of domestic sewage.

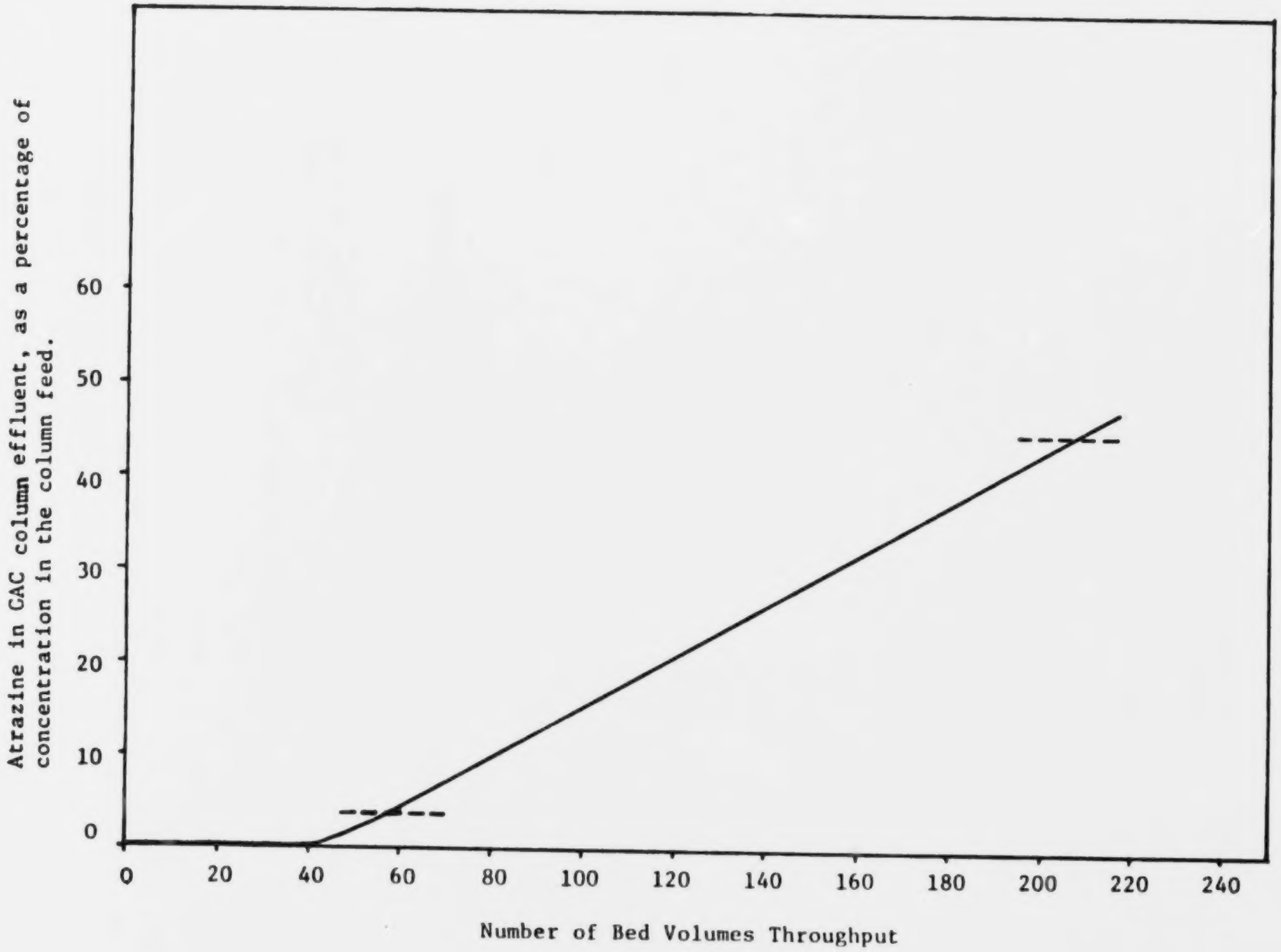


Figure 3. Carbon column treatment of atrazine wastewater - 2nd trial.

Table 5. GAC COLUMN STUDIES, ATRAZINE WASTEWATER
(Column 15.2 cm x 2.2 cm i.d.)

Fraction	Cumulative No. Bed Volumes	Atrazine Concentration	COD mg/l
1	16.6	< 25 ppb	640
2	34.0	< 25 ppb	
3	50.6	92.6 ppb	
4	67.2	1.37 ppm	
5	128.3	NA*	
6	144.8	NA	
7	162.3	NA	
8	181.6	NA	
9	198.2	NA	
10	214.7	16.8 ppm	
Column feed (filtered wastewater)	-	37.7 ppm	1840
Raw wastewater	-	NA	2110

*NA = not analyzed.

Table 6. GAC COLUMN TEST: ATRAZINE WASTEWATER
(Column 15.0 cm x 2.2 cm i.d.)

Fraction	Cumulative Bed Volumes	Concentration of Atrazine in Column Effluent (ppb)
I	12.5	< 25
II	23.5	< 25
III	27.6	< 25
IV	30.5	< 25
V	33.4	< 25
VI	36.2	< 25
VII	47.2	160
VIII	56.4	868

A third column run was conducted in a column 1 1/16 in (i.d.) with a 6 inch depth of activated carbon (39.0 g). One bed-volume equaled 87.2 ml and the flow rate was 12.4 ml/min (0.52 gpm/ft^2). One bed-volume was discarded before collection of the eluate. Results are shown in Table 6 and Figure 4. Detectible levels of atrazine occurred in the effluent between 36 and 47 bed volumes, but were still less than 1 ppm after passage of 56 bed volumes. These results are in general agreement with those of the second run.

In conjunction with these GAC tests, it was noted that in addition to the pesticide present in the wastewater there was a large concentration of surfactants which appeared to be unaffected by GAC treatment. This was indicated by the presence of similar amounts of methanol-insoluble residue in the freeze-dried aliquots of the untreated wastewater and the first fraction collected from the column.

Due to a shortage of liquid for testing, only screening tests of the toxicity to fish of treated and untreated atrazine wastewaters were conducted. While these tests do not have validity of full-scale tests, the GAC treatment appeared to reduce the toxicity (Appendix K).

BIOLOGICAL TREATABILITY STUDIES

Atrazine manufacturing wastewaters were diluted to 8.3% and 16.7% (v/v) with municipal sewage and fed to bench-scale activated sludge units. In the initial phases of the run the wastewater was subjected to primary settling prior to AS treatment. Results, shown in Table 7, indicate that the atrazine was not removed and that the concentration in the effluent ran close to the solubility. In a second run, the unsettled wastewater was fed directly to the units (Table 8). While the influent level in the more concentrated feed was higher, as expected, effluent values still were near solubility levels, probably reflecting removal of excess atrazine onto the sludges. Performance and operating characteristics of the control and test units are shown in Tables 8 and 9 and in Figures 5-7. An analysis of the COD data (Table 10) indicates that the effluent COD from the test units is essentially equal to that contributed by the atrazine wastewater. This possibly indicates that the COD in the atrazine wastewater resists biological oxidation but at this concentration has no deleterious effect on the oxidation of the domestic wastewater components.

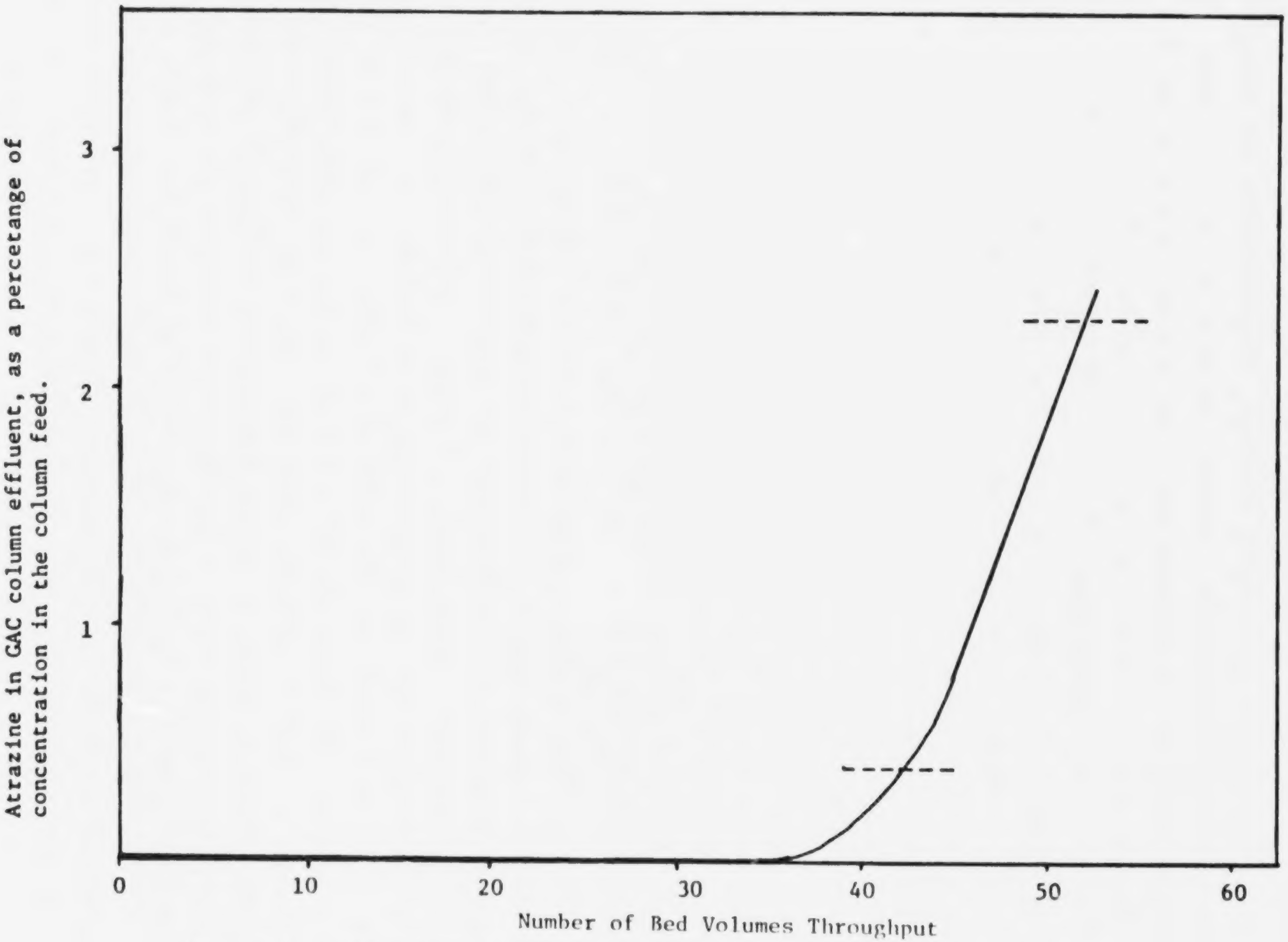


Figure 4. GAC column treatment of atrazine wastewater - 3rd trial.

Table 7. EFFECT OF ACTIVATED SLUDGE TREATMENT OF ATRAZINE WASTEWATER (RUN I)

Sample	Atrazine (mg/l)
16.7% Atrazine Wastewater	
Influent	37 ± 6 (n=3)
Effluent, Unit 1	42
" Unit 2	41
8.3% Atrazine Wastewater	
Influent	28
Effluent, Unit 1	25
" Unit 2	31

Table 8. EFFECT OF ACTIVATED SLUDGE TREATMENT OF ATRAZINE WASTEWATER (RUN II)

Sample	Atrazine (mg/l)
16.7% Atrazine Wastewater	
Influent	60
Effluent, Unit 1	34
" Unit 2	45
8.3% Atrazine Wastewater	
Influent	37 ± 2
Effluent, Unit 1	30
" Unit 2	31
Control	
Influent	ND
Effluent, Unit 1	ND
" Unit 2	ND

ND = < 5 mg/l

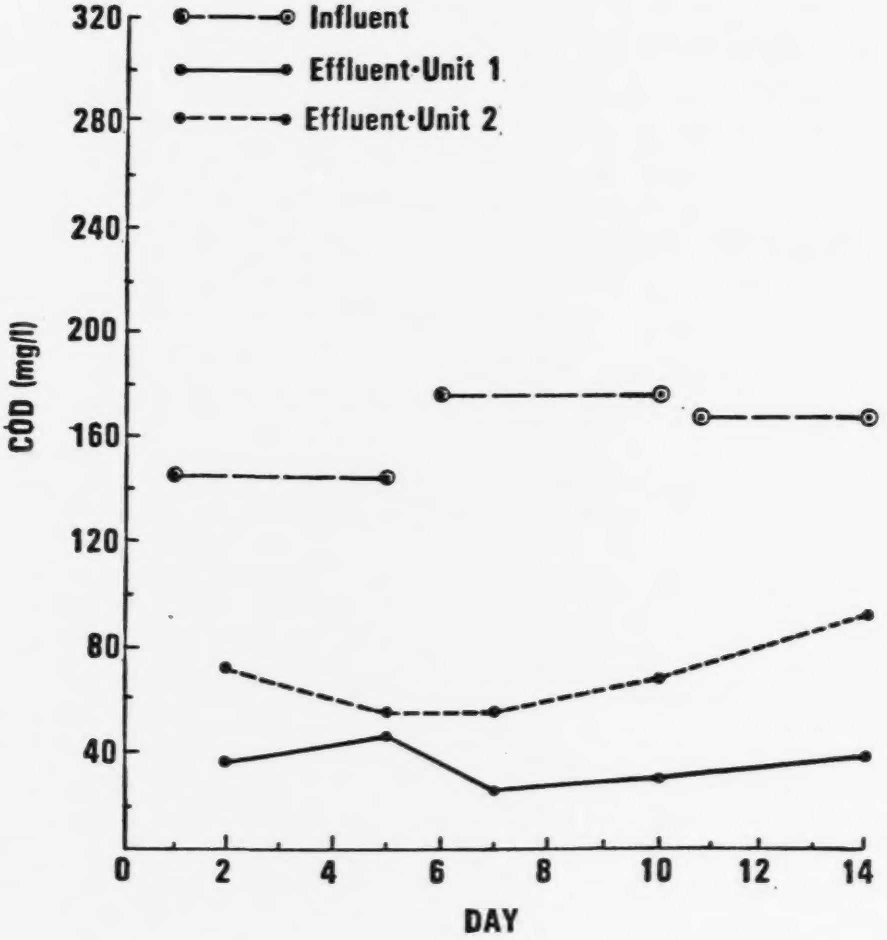


Figure 5. Influent and effluent COD of control activated sludge units.

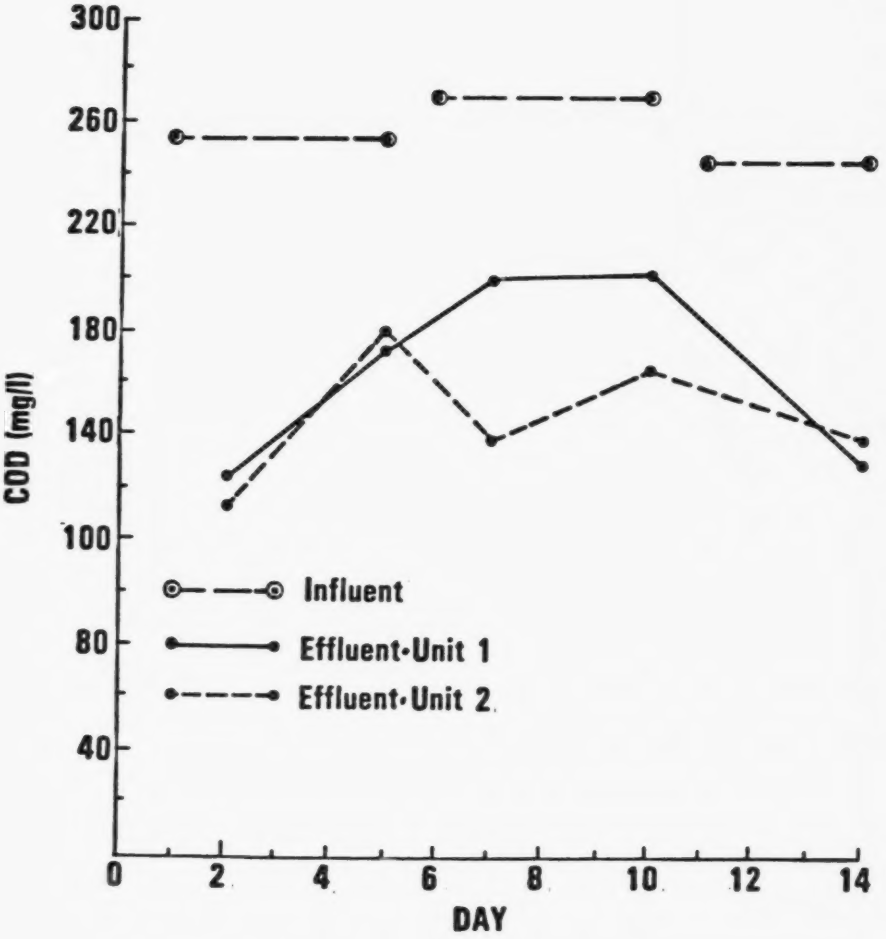


Figure 6. Influent and effluent COD of activated sludge units fed 8.3% atrazine.

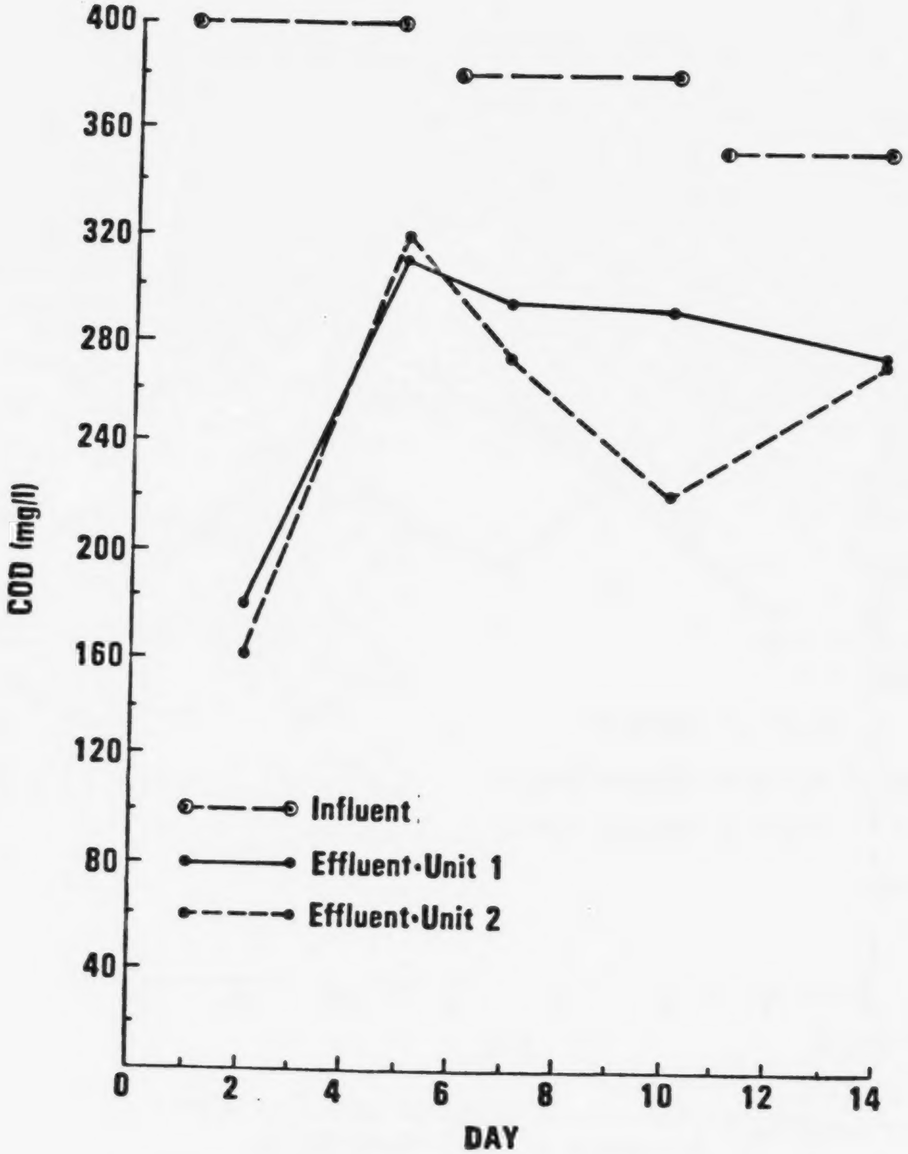


Figure 7. Influent and effluent COD of activated sludge units fed 16.7% atrazine.

Table 9. PERFORMANCE AND OPERATING CHARACTERISTICS OF BENCH SCALE ACTIVATED SLUDGE UNITS, ATRAZINE WASTEWATER SERIES

Parameter	Day	Control			8.3% Atrazine			16.7% Atrazine		
		I	II	av. % removal	I	II	av. % removal	I	II	av. % removal
COD Influent, mg/1	1-5	144	144	-	272	272	-	400	400	-
COD Effluent, mg/1	3	36	72	62	144	132	49	172	152	60
COD Effluent, mg/1	5	48	56	64	192	200	28	312	320	21
COD Influent, mg/1	6-10	176	176	-	288	288	-	380	380	-
COD Effluent, mg/1	7	26	54	77	218	158	35	294	274	25
COD Effluent, mg/1	10	28	64	74	220	184	30	290	220	33
COD Influent, mg/1	11-14	166	166	-	264	264	-	352	352	-
COD Effluent, mg/1	14	36	88	63	148	156	42	272	272	23
Aerator pH	3	6.80	6.58		6.45	6.40		6.70	6.65	
	14	6.50	6.50		6.60	6.55		6.77	6.65	
DO, mg/1	3	5.5	5.9		6.0	5.5		6.2	6.0	
	14	6.1	5.2		6.7	6.6		6.7	5.4	
MLSS, ml/10 ml	1	0.5	0.3		0.5	0.5		0.5	0.6	
	14	0.35	0.23		0.4	0.37		0.5	0.22	

Table 10. ANALYSIS OF CONTRIBUTION OF COD OF ATRAZINE MANUFACTURING WASTEWATER TO COD OF INFLUENTS AND EFFLUENTS OF ACTIVATED SLUDGE UNITS

Unit	Day	COD, mg/l, in excess of that of control units
Influents		
8.3% atrazine waste	1-5	122
	6-10	112
	11-14	98
		ave. 111
16.7% atrazine waste	1-5	256
	6-10	204
	11-14	186
		ave. 215
Effluents*		
8.3% atrazine waste	3	83
	5	144
	7	148
	10	156
	14	90
		ave. 122
16.7% atrazine waste	3	106
	5	264
	7	244
	10	209
	14	210
		ave. 207

*In each case, COD values from the two units are averaged.

Toxicity tests were conducted on untreated and treated domestic and atrazine wastewaters from the first run (Appendix K). In full-scale tests with domestic wastewater there were no deaths at concentrations up to 180 ml/l. As indicated previously, LC_{50} of the untreated full-strength wastewater was 18 ml/l. Influents to the test units contained the wastewater at 8.3% and 16.7% (v/v); stated in terms of dilution, this is equivalent to 1/12 or 1/6 of the original concentration. Therefore the LC_{50} would be expected to be (18 x 12) or 216 ml/l and (18 x 6) or 108 ml/l, respectively. Because of limited availability of effluent, fish toxicity tests were conducted only at concentrations up to 100 ml/l. No significant lethality of either influent or effluents was noted, with the possible exception of one test with a 100 ml/l concentration of effluent from one of the units treating the higher concentration. Since the influents were subjected to primary settling before biological treatment, and were exposed to biological solids during treatment, it is conceivable that the atrazine was sorbed to other material in such a manner that it was no longer available to the fish. Any insoluble atrazine entering the AS unit would be likely to be retained in the sludge. Examination of Tables 7 and 8 indicates that regardless of the amount of atrazine wastewater in the feed, the concentration of atrazine in effluents from the test units varied around the solubility level for atrazine (25-45 mg/l).

Algal assays of influents and effluents from the units receiving the higher concentration of wastewater indicated little or no difference in toxicity of the two. This might be anticipated since biological treatment did not affect soluble atrazine concentration. At concentrations greater than 0.1% (v/v) no algal growth was noted (Appendix K).

Spot tests indicated no inhibition of sewage flora by atrazine wastewater, even at full strength (Appendix O).

In summary, while atrazine wastewater did not seriously interfere with biological treatment, on the other hand, AS treatment failed to remove atrazine.

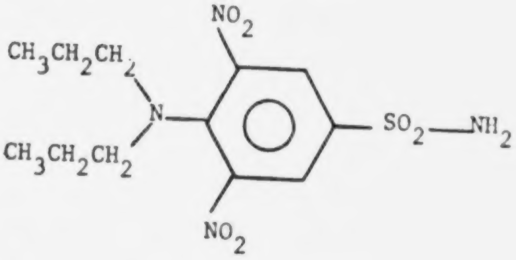
SECTION 5

ORYZALIN WASTEWATER TREATABILITY STUDIES

GENERAL BACKGROUND INFORMATION

Pesticide: Oryzalin CAS No. 19044-88-3
Ryzelan®, Surflan®

Structure



3,5-dinitro-N^4,N^4-dipropylsulfanilamide

Chemical Category

Dinitroaniline, sulfonamide; others of this class include trifluralin, benefin, ethal-fluralin, nitralin, isopropalin, dinitramine, fluchloralin, profluralin, butralin, and penoxalin. Dinitroaniline compounds are also commonly used as dye intermediates.

Properties

M. W. 346.36. Yellow-orange crystalline solid, M.P. 141-142°C. Sol. in H_2O: 2.5 mg/l (25°C). Sol. in polar organic solvents: acetone, methanol, ethanol, acetonitrile. Slightly sol. in benzene and xylene. Insol. in hexane. Vapor pressure $< 1 \times 10^{-7}$ mm Hg at 30°C. No appreciable odor. Not corrosive. Highly soluble in alkaline solutions. May contain colored impurities. Subject to decomposition by ultraviolet irradiation (Dekker and Johnson, 1976).

Intended Use

Herbicide; recommended for weed control in soybeans.
Pre-emergence weedkiller in orchards and vineyards.
"Selective pre-emergence herbicide for control of annual grasses and certain broadleaf weeds in soybeans and other selected crops" (Dekker and Johnson, 1976). Generally formulated as a 75% wettable powder.

Mode of Action

Oryzalin acts on mitochondria to uncouple succinate oxidation at the ADP-limited second stage-4 (IV_2); half-maximal increases in IV_2 oxidation were obtained with 55 μM oryzalin and maximum stimulations at 80 μM with soybean mitochondria. It evidently acts at a site on the energy-transfer system closer to the formation of H_2O than does dinitrophenol or trifluralin (Kirkwood, 1976).

At the whole plant level it inhibits root growth and shoot growth and development (Probst *et al*., 1975).

Manufacturing Information - Introduced in early 1970's

Amount Produced Annually: Unknown

Manufacturer	Location
Sodyeco Division of Martin-Marietta Corp. (for Elanco)	Charlotte, NC

Manufacturing Process

Oryzalin manufacture is operated as a batch process year-round. The manufacturing process shown here is generalized and is not necessarily identical to that at the plant sampled. According to Sittig (1977), a mixture of (3,5-dinitro-4[di(n-propyl) amino] benzenesulfonyl chloride and an excess of concentrated NH_4OH is heated to reflux temperature for several hours and then filtered. The filtrate is concentrated to dryness *in vacuo* and then recrystallized from an acetone-petroleum ether mixture. Synthesis reactions beginning with chlorobenzene may be as depicted in Figure 8 (Dekker and Johnson, 1976).

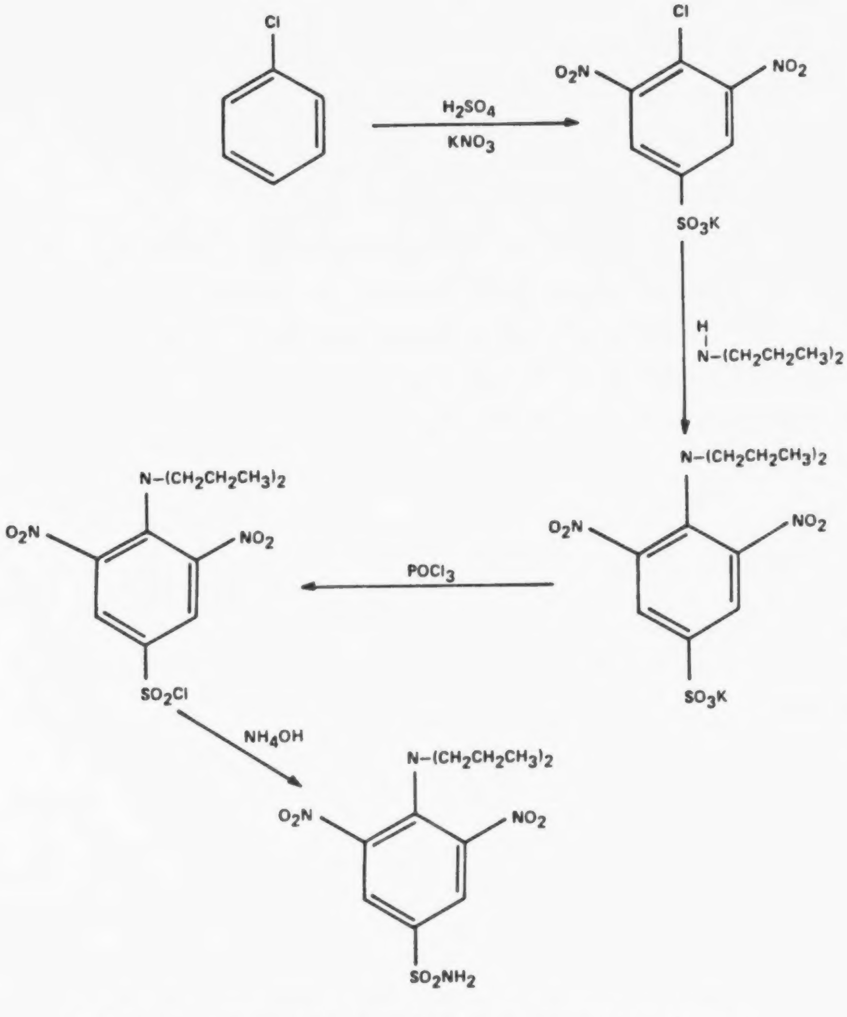

Cl
H2SO4
KNO3
O2N
NO2
SO3K
H
N-(CH2CH2CH3)2
POCl3
SO2Cl
NH4OH
SO2NH2

Figure 8. Possible synthesis of oryzalin from chlorobenzene.

Three major wastestreams are generated in oryzalin production. The major wastewater (I) consists of two aqueous streams containing some filterable solids. This wastewater is highly colored and is presently thermally oxidized. Since this is a very costly process, there is incentive to examine alternative methods of disposal. The second stream (II) is a washwater containing oryzalin at very low levels (low ppb range). This stream is currently discharged to the plant's extended aeration system. The third waste (III) is a tar-like residue containing 10-20% oryzalin; the solids in this stream are incinerated at $\geq$ 1600°F. Streams I and II were examined during the course of this project.

Subsequent to the completion of this project the manufacturer modified the manufacturing process and eliminated the wash step; therefore this wastestream is no longer generated.

Health and Ecological Effects

Toxicity--

Rat, oral, LD_{50}: > 10 g/kg (Fairchild, 1977)
Gerbil, oral LD_{50}: > 10 g/kg
Cat, adult, oral LD_o: > 1 g/kg (Elanco information)
Chicken, adult, oral LD_o: > 1 g/kg "
Dog, adult, oral LD_o : > 1 g/kg "
Fish, bluegill sunfish, TL_{50}, 96 hr: 2.88 mg/l
rainbow trout, TL_{50}, 96 hr: 3.26 mg/l;
"No effect level": 1 mg/l

Of the dinitroaniline herbicides, nitralin and oryzalin are least toxic to fish, while trifluralin is much more toxic with LC_{50}'s ranging from 0.06-0.56 mg/l (Probst et al., 1975).

Mutagenic Potential--

While no information is available on mutagenicity of oryzalin, the related compound trifluralin does not induce point mutations in three microbial systems which have been tested, and there are no reports of oncogenic effects of dinitroaniline herbicides (National Research Council, 1977).

Bioaccumulation and Other Effects--

Probst et al. (1975) state that neither oryzalin nor its metabolites accumulate in the edible portion of tolerant crops and that with the exception of aquatic systems oryzalin is "a pesticide of maximum safety to the environment." Since dinitroanilines are not used for aquatic weed control, entry into aquatic systems would occur only by accident, by runoff from agricultural areas, and by discharge of manufacturing wastewaters, and even then, according to Helling (1976), photodecomposition and sorption to sediments would tend to minimize adverse effects.

CHARACTERIZATION OF WASTEWATERS FROM ORYZALIN PRODUCTION

As indicated above, two wastestreams are generated in oryzalin manufacture (Table 11). The wastewater was heavily colored, corresponding to an absorbance of 420 units. Analysis indicated this to be due not to oryzalin but to a closely related compound. Color was measured by ultraviolet-visible spectroscopy. Measurements of color could not be directly related to concentration of oryzalin itself, as spectra for pure oryzalin and for the wastewater were substantially different. The absorbance maximum of pure oryzalin is 350 nm, as compared to 420-430 nm for the untreated wastewater. The pH was alkaline and the levels of chloride, alkalinity, nitrogen compounds, dissolved solids, and COD were extremely high. The nitrogen occurred primarily as ammonia, and the wastewater had a distinctive ammoniacal smell.

The washwater contained large amounts of organic solvent (toluene), which interfered with certain analyses. This stream was a lighter yellow version of the wastewater and except for the COD, was a more dilute version of that stream.

Note the wide variation in the samples obtained from the manufacturer. The second sample was taken at a time when the plant was not operating efficiently due to problems caused by cold weather. Discussions with plant personnel indicate that wide fluctuations in wastewater characteristics can occur.

Table 11. CHARACTERIZATION OF ORYZALIN WASTEWATERS

Parameter	Washwater Sample 1	Washwater Sample 2	Process Wastewater Sample 1	Process Wastewater Sample 2
pH	9.2	2.2	8.8	9.2
Cl^-, mg/1	730	1,700	27,000	45,000
Alkalinity, mg/1 as $CaCO_3$	0.21	985	960	20,750
TKN, mg/1	97.3;131*	420	25,900	28,700
NH_4-N, mg/1	37;66;75*	30	23,800	28,000
NO_2-N+NO_3-N, mg/1	-	-	-	870
TP, mg/1	0.2	5.8	299	12.5
COD, mg/1	130,500	260,000	36,500	79,000
Sol. COD, mg/1	-	-	79,200	73,000
Suspended solids, mg/1	1.5	-	2,450	368
Total solids, mg/1	-	-	-	73,000
Total dissolved solids, mg/1	184	30,220	-	72,540
Settleable solids, mℓ/1	0		8	12
Oryzalin, mg/1	-	N.D.**	N.D.**	N.D.**

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[*] Interferences made analysis difficult; values shown represent those obtained in replicate analyses.

[**] < 2 ppb

Reported 96 hr LC_{50} values for fish for commercial oryzalin are 2.88-3.26 mg/l. However, unformulated oryzalin obtained directly from the manufacturer failed to kill fish in screening tests (3 fish/jar) at concentrations up to 5 mg/l (Appendix L). Screening tests with the initial actual wastestreams indicated these streams, especially the wastewater, to be highly toxic.

The second (large) sample of oryzalin production wastewater was subjected to toxicity testing with fish and algae. As noted above, oryzalin itself was not detectable in the wastewater; however, the fish toxicity tests showed the wastewater to be highly toxic, with an LC_{50} of 0.3 ml/l (Appendix L).

It is probable that the ammonia content of the wastewater is responsible for the major portion of the toxicity. The ammonia-N contents of the two samples were, respectively, 23,800 and 28,000 mg/l. The toxicity of ammonia is highly dependent on pH, temperature, hardness, and other factors, but concentrations of ∿ 2.5 mg NH_3/l (2.0 mg NH_4-N/l) at neutral pH are generally considered harmful and 96 hr LC_{50} values of 3.24 mg/l have been reported (McKee and Wolf, 1963). The ammonia-N content of the oryzalin wastewater at the LC_{50} concentration of 0.3 ml/l would be 8.4 mg/l. Further indication that ammonia contributed to toxicity was given in screening tests of the wastewater with and without air stripping at high pH (see below, "Effect of Aeration on Oryzalin Wastewater").

Algal assays showed that the wastewater severely inhibited growth at concentrations of 1 and 10%, had some inhibitory effect at 0.01 and 0.1%, and was stimulatory at 0.001% (Appendix L). The washwater was considerably less toxic (Appendix L). Ammonia may be toxic to algae, the toxic concentration being highly dependent on algal species and on environmental factors, or it may serve as a nitrogen source. Concentrations of ∿ 300-400 mg/l (as NH_3-N) have been shown to inhibit growth of diatoms to 50% of the control growth (McKee and Wolf, 1963). The expected NH_3-N concentrations in the test media, along with their effect on algal growth, may be summarized below:

Dilution	NH_3-N, mg/l	Effect
10%	2800	No growth
1%	280	No growth
0.1%	28	Moderate growth
0.01%	2.8	Moderate growth
0.001%	0.28	Growth stimulation

The values are in general agreement with those reported by others.

ACTIVATED CARBON STUDIES

Adsorption Isotherm Studies

Oryzalin wastewater was subjected to adsorption isotherm studies with a variety of carbons and with two resins. Initial studies (Table 12) with 2 g carbon per 100 ml of wastewater indicated that a considerable amount of color was removed but that there was such a large amount initially that the amount remaining was still highly colored. Performance of the resins was poor compared to most of the carbons. Further studies were conducted with those carbons performing best (Table 13 and Figure 9). These studies indicated that the color was readily absorbed onto carbon (note the very large X/M values), but that carbon requirements would be very large.

Liquid adsorption studies were also conducted on the washwater (Tables 14 and 15). Although the color was much less intense, a smaller amount was absorbed per unit weight of carbon, possibly due to the presence of competing organic materials in this wastestream.

Granular Activated Carbon Treatment of Oryzalin Wastewater

Treatability of oryzalin wastewater by GAC was evaluated in column studies with Calgon Filtrasorb 400 carbon. Raw wastewater was filtered through filter paper (Whatman 2V, medium porosity or Millipore prefilter) prior to column treatment.

In initial studies a column with a cross-sectional area of 0.0144 ft^2 was packed to a height of 4 ft with 692.3 g of carbon which had been dried at least 2 hours at 150°C. This carbon was slurried in hot water to expel most of the air, then added to the column in small increments, keeping a thin layer of supernatant liquid present at all times. The bed volume was

Table 12. LIQUID ADSORPTION ISOTHERM DATA FOR ORYZALIN WASTEWATER--SCREENING STUDIES

Carbon (or Resin)	M Wt. of Carbon, g/100 ml of solution	C^* Residual Pesticide, mg/1	X Pesticide Adsorbed, mg/1	X/M Pesticide Adsorbed, Per Unit Weight of Carbon g/g
1. None (control)	0	60,800	0	-
2. Nuchar SA	2.0	32.800	28,000	1.4
3. Nuchar WV-L	2.0	40,900	19,900	1.0
4. RX-WV-L	2.0	39,100	21,700	1.1
5. RX-WV-G	2.0	34,000	26,800	1.3
6. Nuchar WV-G	2.0	36,800	24,000	1.2
7. Calgon Filtrasorb 400	2.0	33,700	27,100	1.4
8. Calgon Filtrasorb 400	2.0	34,100	26,700	1.4
9. Union Carbide LCK	2.0	49,300	11,300	0.6
10. Union Carbide LCL	2.0	52,200	8,600	0.4
11. Dowex 1-X8, 50-100 mesh, chloride form, ion-exchange resin	2.0	48,600	12,200	0.6
12. Amberlide XAD-2	2.0	53,100	7,700	0.4

[*] TLC indicated that the principal chromophores were not oryzalin but two more polar compounds.

Table 13. LIQUID ADSORPTION ISOTHERM DATA FOR ORYZALIN WASTEWATER

Carbon	M Wt. of Carbon, g/100 ml of Solution	C Residual Pesticide, mg/l	X Pesticide Adsorbed, mg/l	X/M Pesticide Adsorbed, Per Unit Weight g/g	X/M at C_o
Control	0	60,300	0	0	
1. Calgon Filtrasorb 400	0.04	52,400	7,800	19.8	
	0.08	54,700	5,600	7.0	
	0.16	52,800	7,500	4.7	
	2.0	37,000	23,300	1.2	~1600
2. Calgon Filtrasorb	0.04	52,800	7,500	18.8	
	0.08	52,400	7,900	9.9	
	0.16	51.300	9,000	5.6	
	2.0	35,200	25,100	1.2	~1750
3. Nuchar SA	0.04	52,800	7,500	18.8	
	0.08	52,400	7,900	9.9	
	0.16	51,600	8,700	5.4	
	2.0	37,800	22,300	1.1	~2100
4. RX-WV-G	0.04	53,900	6,400	16.0	
	0.08	54,600	5,700	7.1	
	0.16	53,500	6,800	4.2	
	2.0	35,900	24,400	1.2	~1650

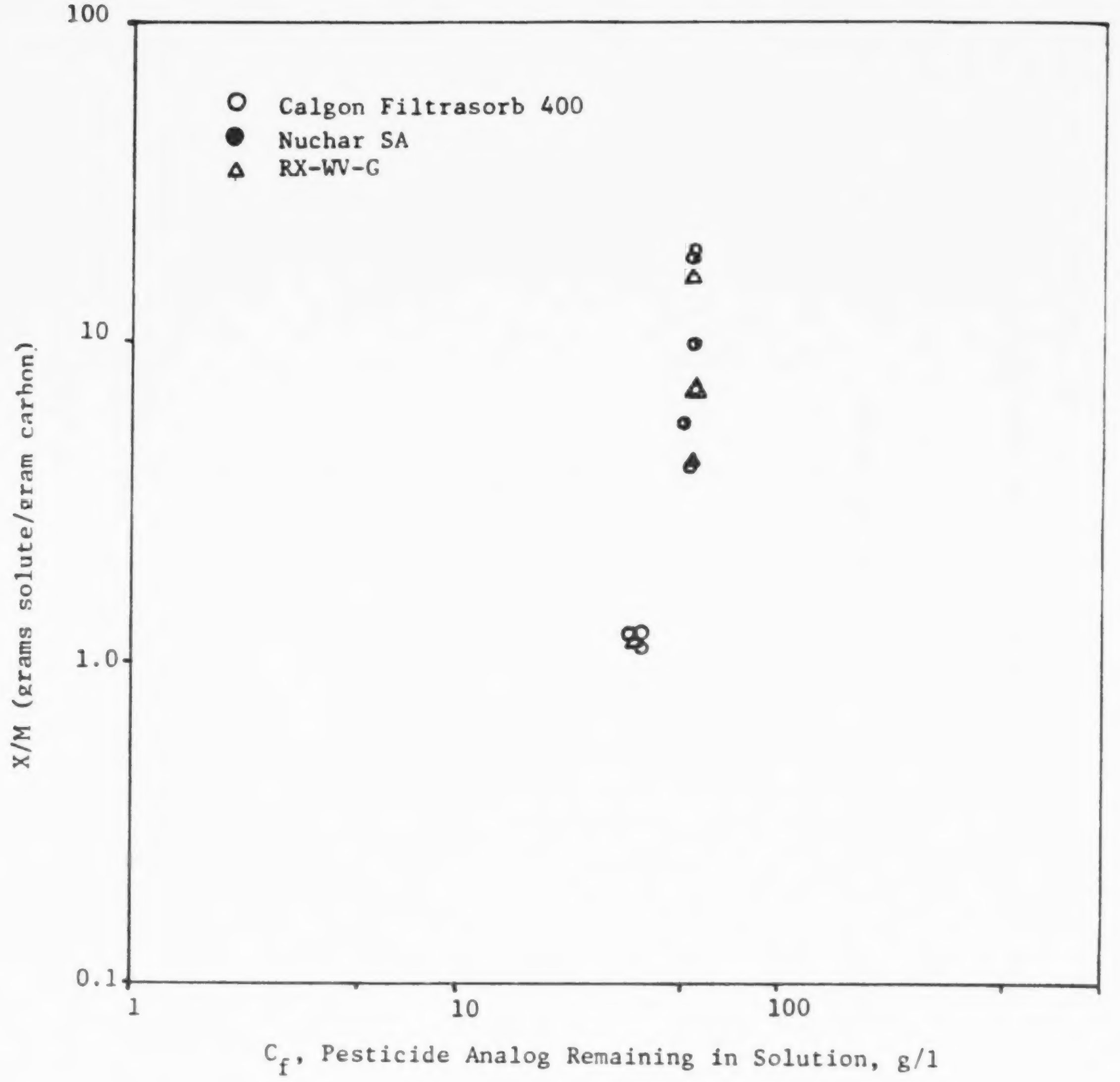


Figure 9. Adsorption isotherm of oryzalin production wastewater.

Table 14. LIQUID ADSORPTION ISOTHERM DATA FOR ORYZALIN WASHWATER--SCREENING STUDIES

Carbon (or Resin)	M Wt. of Carbon, g/100 ml of Solution	C Residual Pesticide, mg/l	X Pesticide Adsorbed mg/l	X/M Pesticide Adsorbed Per Unit Weight g/g
1. None (control)	0	21.2	0	-
2. RX-WV-L	2.0	10.1	11.1	0.0006
3. RX-WV-G	2.0	11.7	9.5	0.0005
4. Nuchar SA	2.0	12.8	8.4	0.0004
5. Nuchar WV-G	2.0	4.1	17.4	0.0009
6. Nuchar WV-L	2.0	8.4	12.8	0.0006
7. Calgon Filtrasorb 400	2.0	2.3	18.8	0.0009
8. Calgon Filtrasorb 400	2.0	1.6	19.6	0.001
9. Union Carbide LCK	2.0	5.3	15.9	0.0008
10. Union Carbide LCL	2.0	5.6	15.6	0.0008

Table 15. LIQUID ADSORPTION ISOTHERM DATA FOR ORYZALIN WASHWATER

Carbon	M Wt. of Carbon, g/100 ml of Solution	C Residual Pesticide, mg/l	X Pesticide Adsorbed mg/l	X/M Pesticide Adsorbed Per Unit Weight g/g
Control	0	0.142	-	-
1. Nuchar WV-C	0.04	0.092	0.05	1.25×10^{-4}
	0.08	0.085	0.057	7.12×10^{-5}
	0.16	0.033	0.109	6.81×10^{-5}
	2.0	0.002	0.140	7.0×10^{-6}
2. Calgon Filtrasorb 400	0.04	0.098	0.044	1.1×10^{-4}
	0.08	0.070	0.072	9.0×10^{-5}
	0.16	0.019	0.123	7.7×10^{-5}
	2.0	0.000	0.142	7.1×10^{-6}
3. Calgon Filtrasorb 400	0.04	0.091	0.050	1.25×10^{-4}
	0.08	0.074	0.068	8.5×10^{-5}
	0.16	0.031	0.111	6.9×10^{-5}
	2.0	0.0	0.142	7.1×10^{-6}

1600 ml. Filtered wastewater was pumped through the column at 36 ml/min (0.65 gpm/ft^2). Two runs were conducted, one at the pH of the filtered wastewater and the other after adjustment to pH 6. Breakthrough was indicated by appearance of color in the column effluent. Spectra of each fraction were obtained with a Perkin-Elmer 402 visible spectrophotometer. Results are shown in Table 16 and in Figures 10-12. GAC treatment was capable of completely removing color of the wastewater and in reducing the COD by > 95%. At the pHs tested, adjustment of pH of the column feed had little or no effect on GAC treatment. The results indicate that GAC column treatment is completely capable of high levels of treatment of this wastestream insofar as color and COD are concerned. Unfortunately, as anticipated from results of the isotherm tests, the carbon requirements are exceedingly high, with breakthrough of color and COD occurring somewhere between 1.5 and 2.0 bed volumes.

As noted previously, color was due largely to non-oryzalin components. Note the shift of wavelength maxima which occurred with breakthrough (Figure 11). This shift is indicative of a multicomponent mixture, which was verified by thin-layer chromatography. On TLC analysis more than five components, varying in color from pale yellow to rose, were observed. Assuming that the color in the oryzalin wastewater will reach breakthrough in $\sim$ 5 bed volumes, indicated carbon requirements are 86.5-89.3 g/l (720 lb/1000 gal). This requirement is large in comparison with usual industrial requirements of 50-400 lb/1000 gal.

More oryzalin wastewater was carbon treated in a second trial. The column was 2.5 cm (i.d.) and was packed to a depth of 120 cm with carbon (286 g). The bed volume was 618 ml and the flow rate was 10.0 ml/min (0.48 gpm/ft^2). A void volume of 600 ml of liquid was discarded before fractions of the eluate were collected. Spectra of each fraction were obtained as above. Results are shown in Table 17. Results (COD, color removed) were comparable to those obtained in the first trial.

Algal assays of the treated wastewater indicated that the inhibitory effects at 1 and 10% (v/v) concentrations still persisted, whereas at lower concentrations there was little difference from control growth (Appendix L).

Table 16. EFFECT OF GAC TREATMENT ON ORYZALIN WASTEWATER AT pH 6 AND pH 9

Sample	Fraction	Cumulative Bed Volumes	Absorbance Units	Color Remaining, %	COD, mg/l
	Untreated, unfiltered	0	-	-	57,020
pH 9	Column influent	0	632	-	58,600
	Effluent I	1.77	0	0	2,160
	Effluent II	2.67	1.45	0.23	27,200
	Effluent III	4.64	22.4	3.49	
	Effluent IV	7.01	45.3	7.1	
pH 6	Column influent	0	545	-	65,740
	Effluent I	1.56	0	0	2,320
	Effluent II	2.18	0.20	0.04	44,000
	Effluent III	4.55	0.65	0.12	
	Effluent IV	6.90	42.9	7.87	

Table 17. EFFECT OF GAC TREATMENT ON ORYZALIN WASTEWATER

Fraction	Cumulative Bed Volumes	Absorbance Units	Wavelength of maximum, nm	COD, mg/l (avg. of 2)
Untreated, unfiltered	0	0	-	78,250
Column feed	0	420	426	72,500
Effluent I	1.55	0	-	2,800
Effluent II	2.09	0	-	-
Effluent III	2.49	0	-	-
Effluent IV	3.32	0	-	-
Effluent V	4.87	0.725	405	-
Effluent VI	5.48	3.50	405	-

- = not analyzed

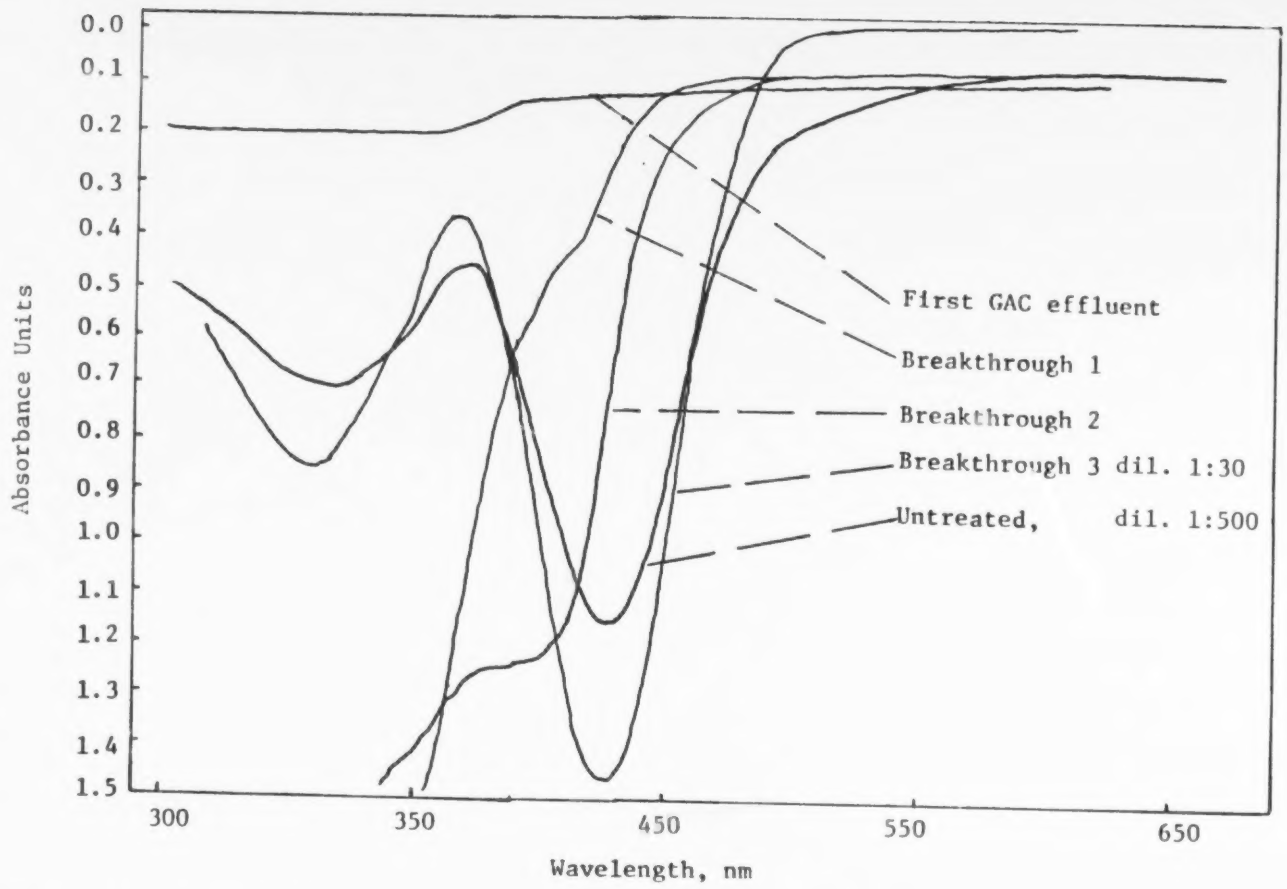


Figure 10. Absorbance of effluent from GAC column treating oryzalin production wastewater, pH 6; breakthrough of color at progressively larger cumulative bed volumes is indicated.

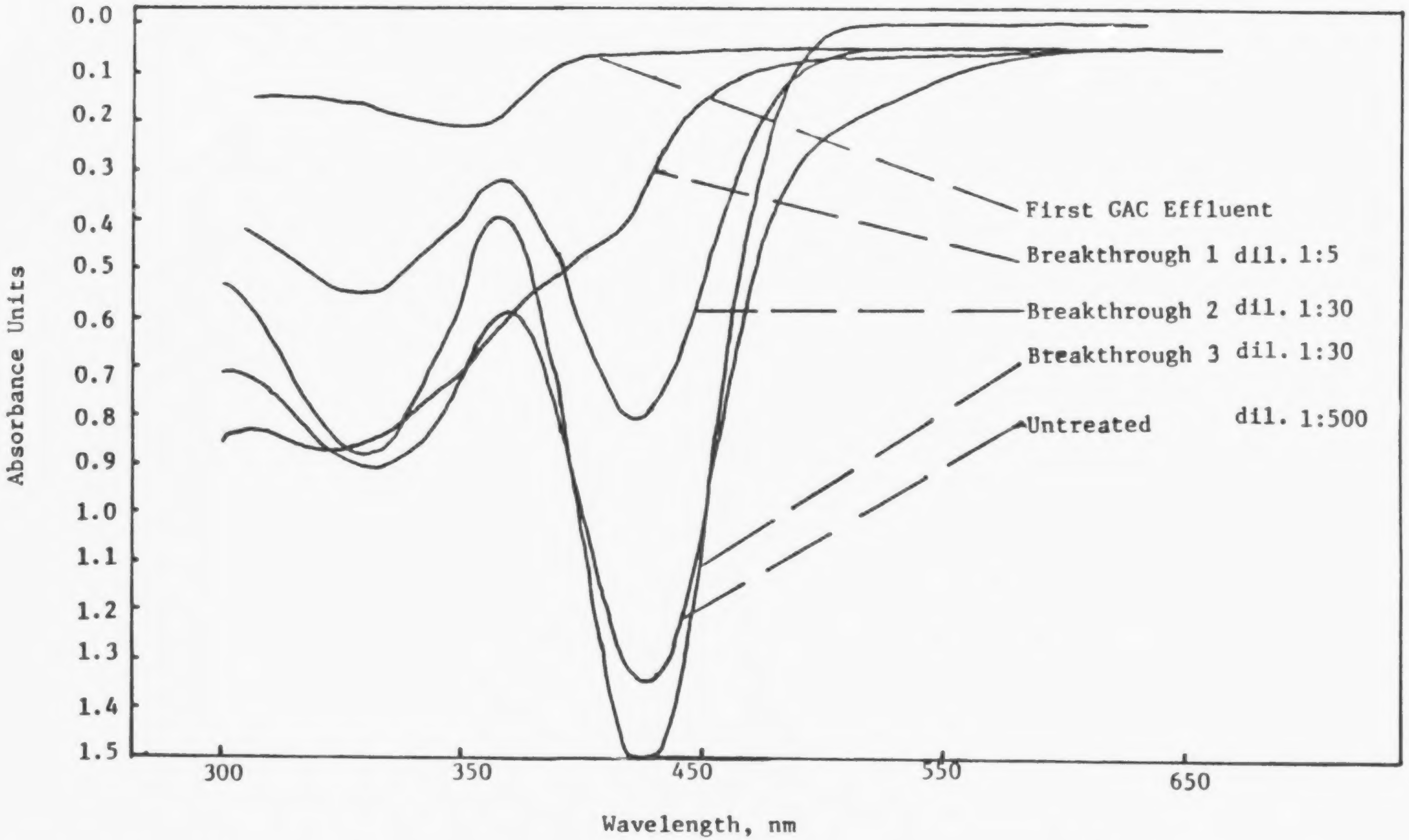


Figure 11. Absorbance of effluent from GAC column treating oryzalin production wastewater, pH 9. Breakthrough of color at progressively larger cumulative bed volumes is indicated.

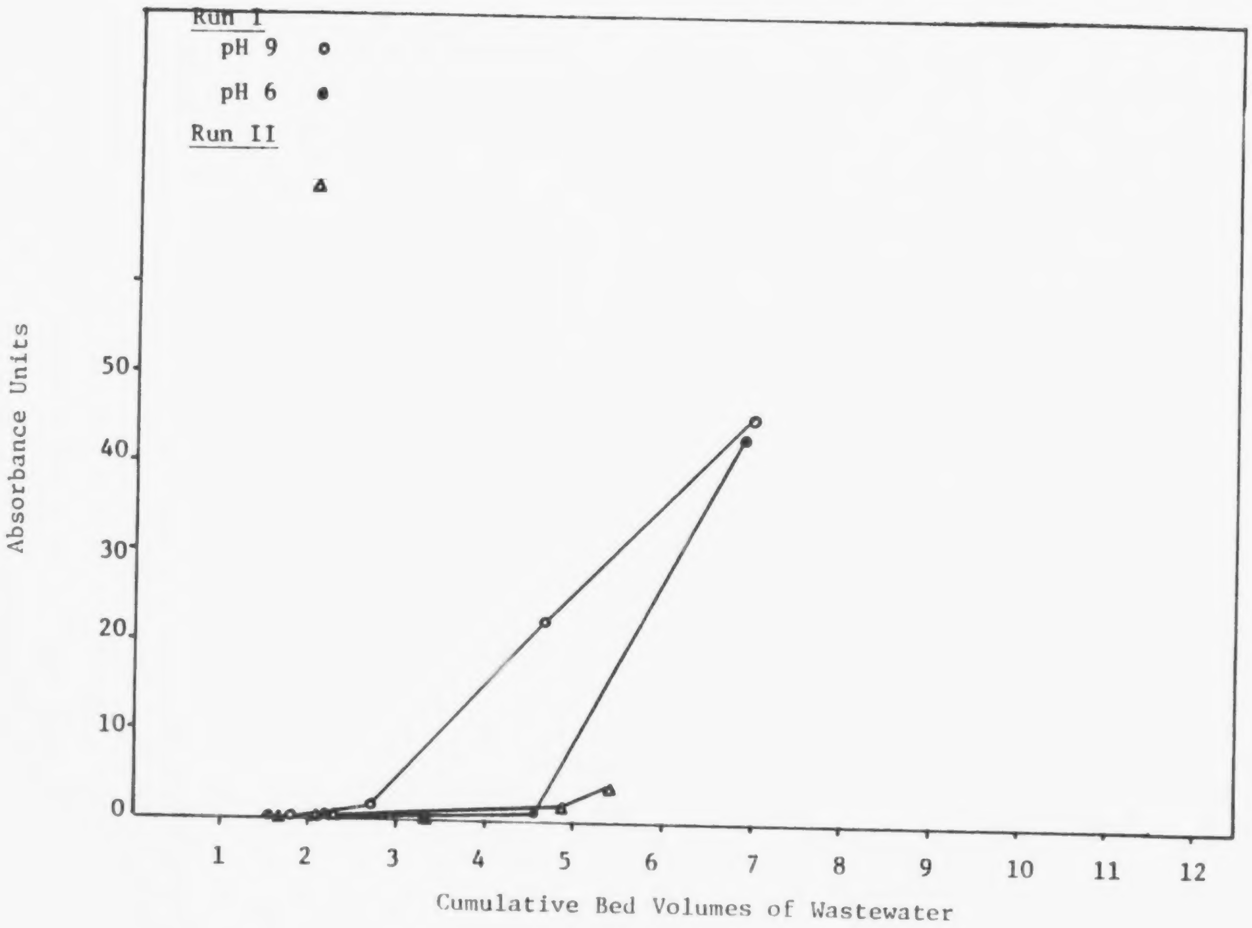


Figure 12. GAC column treatment of oryzalin manufacturing wastewater, pH 9 and pH 6.

Since all the color had been removed from the wastewater by the GAC treatment, it is probable that the toxic component was not oryzalin or its analogs, but some other component, possibly ammonia.

Fish assays of the GAC treatment wastewater (Appendix L) indicated that toxicity of oryzalin wastewater was not substantially reduced by carbon treatment. Complete mortality was noted at concentrations of 1.0 ml/l and greater. It was hypothesized that ammonia still present in the carbon column effluent contributed to the toxicity of GAC treated effluent. To test this hypothesis a second bioassay was conducted with carbon column effluent subjected to ammonia stripping, as reported below.

BIOLOGICAL TREATABILITY STUDIES OF ORYZALIN MANUFACTURING WASTEWATER

Bacterial spot tests with both oryzalin wastewater and washwater streams indicated that the undiluted streams were markedly inhibitory to sewage flora (Appendix O). Oxygen uptake studies (Appendix P) also indicated that at a 10% (v/v) concentration, the wastewater severely inhibited respiration by unacclimated activated sludge (AS), whereas a 1% concentration (v/v) caused much less inhibition.

Nevertheless, biological treatability studies were attempted at both 1 and 10% (v/v) feed concentrations. In both cases, the AS units failed to operate. At the higher concentration, the test units rapidly lost all of the sludge to the effluent. When it became apparent that a 10% concentration would not be tolerated, another series of tests was set up at 1%. The units failed to operate satisfactorily, again exhibiting loss of sludge from the reactor. In terms of COD removal performance characteristics of the control and test units are shown in Table 18 and in Figures 13 and 14. Operational characteristics are shown in Table 19. Despite operational difficulties it was noted that substantial reductions in COD were occurring (Table 18). Since there could be little or no biological activity responsible for these removals, additional tests (described below) were conducted to determine if aeration alone could be responsible, for example, by volatizing or oxidizing the pesticide or other organic components.

It is noteworthy (Table 19) that while the pH of the mixed liquor in the control units (those receiving only domestic sewage feed) dropped below

Table 18. PERFORMANCE CHARACTERISTICS OF BENCH SCALE ACTIVATED SLUDGE UNITS - ORYZALIN WASTEWATER SERIES

Dates	Control				Oryzalin Wastewater				Oryzalin Wastewater		
	Influent COD mg/1	Effluent COD mg/1		% Removal Average	Influent COD mg/1	Effluent COD mg/1		% Removal Average	Influent COD mg/1	Effluent COD mg/1	
		I	II			I	II			I	II
1-6	265			88					7,800		
2		35	31	88							
											1,880 1,720
4		32	32	78							
7-14	120			62	1,660						
7		28	24	*							
9		14	79	*		800	410	64			
11		238	35	79		940	440	30			
14		106	40			504	464	29			
15-17	183				1,090						
16		32	44			425	480	63			

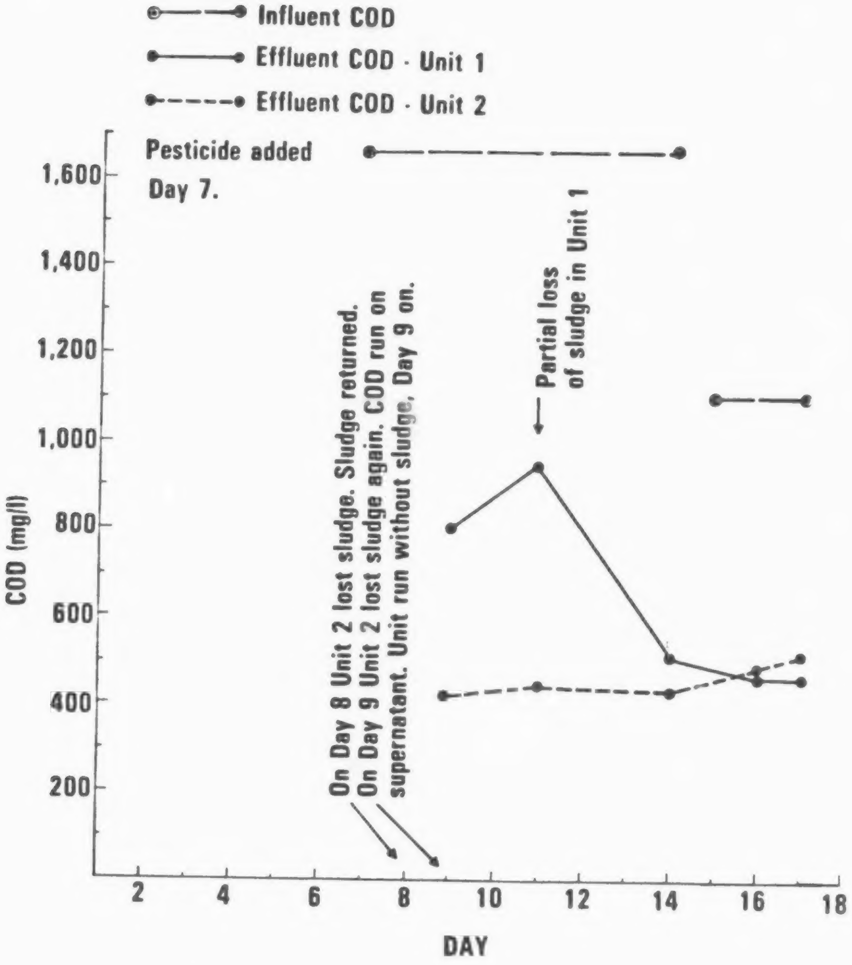
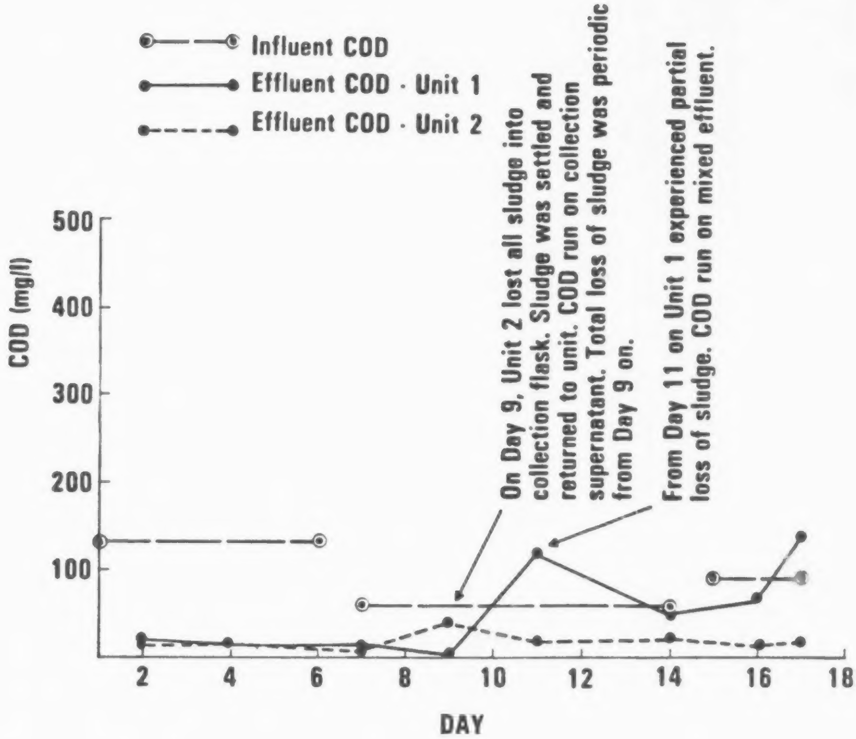


Figure 13. Influent and effluent COD for activated sludge units fed 1% oryzalin.



On Day 9, Unit 2 lost all sludge into collection flask. Sludge was settled and returned to unit. COD run on collection supernatant. Total loss of sludge was periodic from Day 9 on.

From Day 11 on Unit 1 experienced partial loss of sludge. COD run on mixed effluent.

Figure 14. Influent and effluent COD for control activated sludge units fed primary settled wastewater alone.

Table 19. OPERATING CHARACTERISTICS OF BENCH SCALE ACTIVATED SLUDGE UNITS - ORYZALIN WASTEWATER SERIES

Parameter	Day	Control		Oryzalin, 1%		Oryzalin, 10%	
		I	II	I	II	I	II
DO, mg/1	1	5.7	5.8			7.4	6.8
	9	7.2	7.3	7.2	7.4		
	15	7.1	7.1	6.7	6.6		
pH	1	7.4	5.9			8.5	8.5
	8	5.6	5.7	8.0	8.1		
	16	6.8	6.1	8.2	8.1		
MLSS, ml/10 ml	1	0.4	0.5			0.2	0.4
	9	0.4	0.2	0.2	0.0		
	15	0.1	0.15	0.1	0.0		
	17	0.15	0.05	0.1	0.0		

neutral, that of the test units remained above pH 8. Such a drop in pH is generally associated with nitrification and its failure to occur in the test units may be indicative of interference of the wastewater with nitrification. Further studies would be necessary in order to confirm or disprove this conjecture.

Fish bioassay studies indicated that the LC_{50} of the untreated wastewater containing 1.0% oryzalin wastewater was 60 ml/l (Appendix L). This was in agreement with the LC_{50} value of 0.3 ml/l of the undiluted wastewater, since it can be calculated that the LC_{50} of the 1% dilution would be 30 ml/l. After AS treatment, the wastewater was not toxic at levels up to 180 ml/l (Appendix L), indicating that some mechanism occurring in the units removed the toxicity.

Effect of Aeration on Oryzalin Wastewater

Although presence of oryzalin wastewater, even as low as 1%, caused failure of bench scale activated sludge units, it was noted that some COD removals were being obtained, evidently by a nonbiological process. Consequently, the effect of simple aeration on COD levels in oryzalin-supplemented primary domestic sewage was determined. Two different samples of primary sewage were used and oryzalin wastewater was added to a final concentration of 1%. The solutions were aerated for 8 hr with compressed air (humidified by bubbling through water). Before and after aeration, aliquots were removed for COD analysis. In one sample, the COD was reduced from 952 mg/l to 476 mg/l; in the other, from 913 mg/l to 436 mg/l. These results indicate that some oxygen-demanding components of the oryzalin wastewater, responsible for 50-52% of the COD, can be removed by air-stripping (or oxidation).

Further aeration tests were conducted at high pH with untreated, filtered, and GAC treated wastewater to determine if conditions favorable for air-stripping of NH_3 would moderate toxicity of the wastewater to fish. Although the amount of sample was only sufficient for screening tests, survival of fish at a wastewater concentration of 1.0 ml/l was consistently greater when the wastewater had been pretreated by aeration at high pH (Table 20). Note that at the 1 ml/l (0.1%) concentration survival of fish in carbon column effluents was markedly improved by air stripping.

Table 20. SCREENING TESTS: EFFECT OF AMMONIA STRIPPING ON TOXICITY OF ORYZALIN WASTEWATER TO FISH.

Sample	Wastewater Concentration, ml/l	No. fish surviving at indicated time (Initial = 3)	
		24 hr	96 hr
Control		3	2
Untreated	0.1	3	3
	0.32	3	3
	1.0	0	0
Filtered, Whatman 2V	0.1	3	3
	0.32	3	2
	1.0	0	0
GAC, 1st harvest not stripped	0.1	2	1
	0.32	3	3
	1.0	0	0
stripped	0.1	3	3
	0.32	3	3
	1.0	3	3
GAC, Breakthrough (Fraction IV) not stripped	0.1	3	3
	0.32	3	3
	1.0	0	0
stripped	0.1	3	3
	0.32	3	3
	1.0	3	2

Conditions for stripping: pH was raised to ∿ 11.2 with NaOH solution; solution was aerated for 2 hr; pH was readjusted to 8.5.

Overall, the results of the AS and air stripping tests indicated that simple aeration for 6-8 hr removed much of the COD and greatly moderated the toxicity to fish of the oryzalin wastewater and that short-term air stripping at high pH also moderated the toxicity. No significant changes in color of the solutions were noted. These results indicate that aeration processes should be further investigated for eliminating toxicity and reducing oxygen demand of wastewaters from oryzalin manufacture. Pre-aeration might possibly improve performance of AS treatment by removing toxic materials, reducing excess oxygen demand, or lowering NH_3 levels. By removal of some of the organic material, it might also improve GAC treatment.

EFFECT OF ULTRAVIOLET IRRADIATION ON EFFLUENT FROM ORYZALIN MANUFACTURE

Since oryzalin is reportedly degraded by ultraviolet (UV) irradiation, an experiment was conducted at high levels of irradiation to determine if significant color removal could be obtained. A 200 ml aliquot of oryzalin effluent was irradiated with UV light for a period of 2 hrs. The UV light source was a Hanovia High-Pressure Quartz Mercury Vapor Lamp with the following specifications: lamp watts, 450; arc inches, 4.5; lamp volts, 135; lamp amps, 3.6. The lamp was enclosed in a water-cooled quartz casing which was inserted into a glass tube containing the sample. Sample thickness in the direct path of the light was ∿ 4.5 mm. A small area at the base of the tube received only indirect UV light. A Teflon stirring bar placed in the sample facilitated mixing. Temperature of the sample ranged from 26-28 C. Aliquots (10 ml) were removed at 15 min intervals during the first hour and at the end of the second hour. Due to the high levels of color, these were diluted to 0.25% solutions before spectrophotometric analysis at 300 nm (Bausch and Lomb Spectronic 20). The results are shown in Table 21. Since no color removal was obtained under these conditions (2 hr. at 450 watts) it was concluded that large scale ultraviolet irradiation in commercial units, which generally provide much shorter exposure times, would not be practical for removing color (and, thus, presumably some of the organic components) from this wastewater. It should be remembered, however, that the toxicity of this wastewater is not directly correlated with its color and/or oryzalin content.

Table 21. EFFECT OF ULTRAVIOLET IRRADIATION ON ORYZALIN WASTEWATER

Sample No.	Irradiation Exposure (min)	% Transmittance
1	0	13
2	15	13
3	30	13
4	45	15
5	60	15
6	120	13

SECTION 6

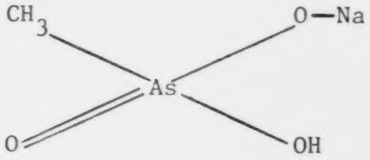
MSMA WASTEWATER TREATABILITY STUDIES

GENERAL BACKGROUND INFORMATION

Pesticide: MSMA CAS No. 2163-80-6

Ansar^{TM}170; Bueno^{TM}; Phyban^{TM}; Daconate^{R}; Silvisar^{R}; Weed-E-Rad^{R}

Structure



Monosodium methanearsonate; sodium acid methanearsonate; methanearsonic acid monosodium salt.

Chemical Category

Organoarsenical; others in this class include methanearsonic acid (MAA), disodium methanearsonate (DSMA), and cacodylic acid (CA).

Properties

M. W. 161.96; highly water soluble; solid, often marketed as a clear, odorless solution at several concentrations such as 51% MSMA.

Intended Use

Herbicide for post-emergence control of weeds in cotton and turf. Controls over 80 species of common weeds (Woolson, 1976).

Mode of Action

MSMA kills sensitive plants following foliar uptake and translocation. It kills relatively slowly, apparently by inhibition of enzymes and thus inhibition of growth (Woolson, 1976). Atrazine has been shown to facilitate uptake of arsenic and since atrazine has a residual action of several months in soil, these residues may enhance action of MSMA (Woolson, 1976).

Manufacturing Information - Introduced 1956

Estimated amount produced annually: 15.9 x 10^3 metric tons in 1974 (Archer *et al*., 1978).

Manufacturer	Location
Diamond Shamrock Corp.	Pasadena, TX
Crystal Chemical Co.	Houston, TX
Vineland Chemical Co.	Vineland, NJ

Health And Ecological Effects

Toxicity:--

Rat, oral, LD 50: 700 mg/kg (Fairchild, 1977)
900 mg/kg (Martin and Worthing, 1974)

Mammalian, LD 50: 50 mg/kg (Fairchild, 1977).

Bluegill sunfish (*Lepomis macrichirus*), LC_{50}, 48 hr: > 1000 mg/l, but presence of surfactants causes increase in toxicity (Martin and Worthing, 1974).

Fathead minnow (*Pimephales promelas*), LC_{50}, 96 hr, >510 mg/l [Southwest Research Institute (SRI), 1979].

Sheepshead minnow (*Cyprinodon varigatus*), LC_{50}, 96 hr, >510 mg/l (SRI, 1979).

Grass shrimp (*Palaemonetes pugis*), LC_{50}, 96 hr, 510 mg/l (SRI, 1979).

Worker bees, newly emerged (*Apis mellifera* L.), 100 ppm (wt basis) is extremely toxic (Woolson, 1976).

Mutagenic Potential--

Does not cause point mutations in *Salmonella typhimurium* strains, T 4 bacteriophage, *E. coli* B host, or *E. coli* KB. (Anderson *et al*., 1972).

Negative response in the following *in vivo* and *in vitro* mutagenesis tests: Ames test, with and without microsomes; *Escherichia coli* WP 2, with and without microsomes; *Saccharomyces cerevisiae* mitotic recombination, with and without microsomes; E. coli, relative toxicity; Bacillus subtilus, relative toxicity; and UDS DNA repair, with and without microsomes (Simmon et al., 1977).

Movement from treated weeds or soil to water is "likely to be minimal because of fixation phenomena to plants, soils, and sediments" (Woolson, 1976).

Fate In Soil--

Certain soil microorganisms are able to metabolize MSMA via carbon arsenic bond cleavage (Kaufman and Kearney, 1976). Arsenic is capable of alkylation and subsequent dealkylation, so the process may be cyclic in nature, the form of arsenic being governed by oxygen tension (Kearney and Kaufman, 1975). According to Woolson (1976), the organic portion of MAA can be metabolized in soil, and the arsenical portion may be reduced to form a volatile compound which can escape to the air. Degradation of the methyl carbon appears to require presence of other organic material (co-metabolism). Dimethylarsine has been found in the air over MSMA treated soils, under both aerobic and anerobic conditions, with 0.8-12.5% of the MSMA being degraded over a 160 day period.

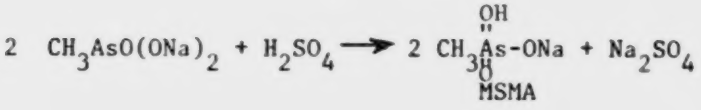
Woolson (1976) also notes that the herbicidal effects are ultimately eliminated by formation of insoluble salts, adsorption on soil colloids, or ion exchange reactions of soils. These processes are dependent on soil type, clays, such as kaolinite, being the most effective.

Manufacturing Process

The manufacturing process described here is generalized and it cannot be assumed that this exact procedure is utilized at the plant site sampled. The reactions are as follows (Sittig, 1977):

$$As_3O_3 + 6\ NaOH \rightarrow 2\ Na_3AsO_3 + 3\ H_2O$$

$$Na_3AsO_3 + CH_3Cl \longrightarrow \underset{\text{DSMA}}{CH_3AsO(ONa)_2} + NaCl$$



$$2\ \ CH_3AsO(ONa)_2 + H_2SO_4 \longrightarrow 2\ \underset{\text{MSMA}}{CH_3\overset{OH}{\underset{O}{As}}\text{-}ONa} + Na_2SO_4$$

DSMA is also a pesticide, but since it is not as soluble as MSMA and must be applied at higher rates than MSMA, its use is not as great (Sittig, 1977).

The production and waste schematic are shown in Figure 15 (from Sittig, 1977).

Current Waste Disposal Practice

Diamond Shamrock, Greens Bayou, TX, treats its wastewaters by clarification, equalization, filtration, carbon filtration and aeration.

CHARACTERIZATION OF MSMA WASTEWATER

The wastewater from MSMA manufacture consists of evaporater distillate. Wastewater samples obtained appeared very clear, resembling tap water. According to the manufacturer, the wastestream is of a highly variable composition.

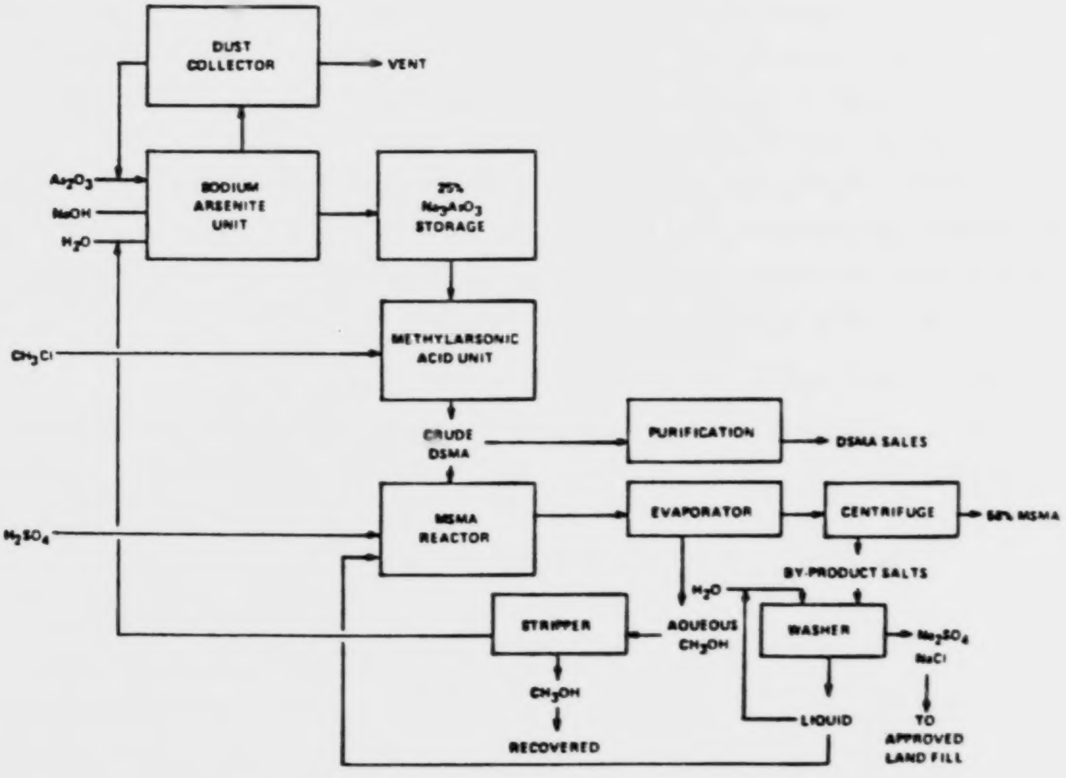

DUST COLLECTOR
VENT
As_2O_3
NaOH
H_2O
SODIUM ARSENITE UNIT
25% Na_3AsO_3 STORAGE
CH_3Cl
METHYLARSONIC ACID UNIT
CRUDE DSMA
PURIFICATION
DSMA SALES
H_2SO_4
MSMA REACTOR
EVAPORATOR
CENTRIFUGE
58% MSMA
BY-PRODUCT SALTS
H_2O
STRIPPER
AQUEOUS CH_3OH
WASHER
Na_2SO_4
NaCl
CH_3OH
RECOVERED
LIQUID
TO APPROVED LAND FILL

Figure 15. Production and waste schematic for MSMA.

Two samples of MSMA manufacturing wastewater were obtained from the manufacturer at a 3 month interval. The two samples varied considerably in solids, COD, and nitrogen content (Table 22). Analysis of the samples indicated that much of the organic content was due to methanol, which was present at concentrations of 3330 and 1600 mg/l. Arsenic content was 22.3 mg/l in the second sample. As described in the materials and methods section, it was necessary to devise a method for measuring the MSMA molecule alone, rather than as arsenic.

Methanol is a relatively common constituent of wastewaters from synthetic chemicals production. It is readily utilized by many microorganisms as a source of carbon and energy and is not considered difficult to treat in biological treatment systems. The arsenic levels in the wastewater, as would be expected, are higher than most industrial wastewaters.

Table 22. CHARACTERIZATION OF MSMA WASTEWATER

Parameter	Sample 1	Sample 2
pH	5.0	4.7
Cl^-, mg/l	350	11
Acidity to pH 8.3, mg/l as $CaCO_3$		18.5
TKN, mg/l	1.3	14.0
NH_4-N, mg/l	0.8	11.2
NO_2-N + NO_3-N, mg/l		<2
TP, mg/l	1.2	3.0
COD, mg/l	9,900	4,100
Suspended solids, mg/l		8
Total Solids, mg/l		60
Total Dissolved solids, mg/l		52
Settleable Solids, mg/l		<0.01
MSMA, mg/l		5.3
Arsenic, mg/l		22.3
Methanol, mg/l	3,300	1,600

Toxicity tests were conducted on the untreated wastewater (Appendix 13). Algae failed to grow in media containing 10% (v/v) MSMA wastewater but at levels of ∼ 3% or less growth was approximately that of the control. This implies that little or no effect on algal growth would be anticipated if the wastewater were diluted by 30-fold.

A screening test of toxicity of the wastewater to fathead minnows was conducted at test concentrations of 100, 180, and 320 ml/l (10, 18, and 32%). After 16 hr all fish in the two higher concentrations were dead. Dissolved oxygen had dropped to 1.5 mg/l, possibly due to bacterial degradation of the large amount of methanol present in the waste. To test this hypothesis and to eliminate the confounding of MSMA toxicity with the stress of low oxygen concentration, a second screening test was conducted at 180and 320 ml/l concentrations. In each case one set of jars was aerated with compressed air and the other set was not aerated. The results gave some indication that aeration reduced toxicity at the 180 ml/l concentration. Due to insufficient quantities of the MSMA wastewater, this test could not be repeated with a large scale assay.

Examining the reported toxicity to fish of two of the MSMA wastewater components, methanol and arsenic, indicates that levels of As showing toxic effects in < 6 days are ≥ 1 mg/l and that fish in general are very tolerant to methanol, some being able to tolerate as much as 8100 mg/l for 24 hours or more (McKee and Wolf, 1963).

ACTIVATED CARBON TREATABILITY STUDIES

Because of time constraints, MSMA was subjected to GAC column treatment directly, without preliminary isotherm studies. An activated carbon column 2.7 (i.d.) and 15 cm long was prepared with Calgon Filtrasorb 400. Due to the clarity of the wastewater, it was not prefiltered. It was pumped through the column at a flow rate of 750 ml/hr (0.535 gpm/ft^2). One bed volume (87.2 ml) was discarded before collecting fractions. Results are shown in Table 23 and in Figure 16. Note that at <12 column volumes the COD level was approaching that of the feed and the MSMA level was greater than 1 mg/l (as As). Thus, carbon treatment appears to be not very promising for treating this

Table 23. EFFECTIVENESS OF GAC TREATMENT FOR REMOVAL OF MSMA FROM MANUFACTURING WASTEWATER

Sample	Cumulative No. of Column Volumes	MSMA in mg/l as As	COD mg/l (avg. of 2 values)
Effluent, fraction I	11.5	1.8	2,115
Effluent, fraction II	22.6	3.3	-
Effluent, fraction III	35.3	3.7	-
Effluent, fraction IV	47.9	3.8	-
Effluent, fraction V	58.9	3.8	-
Effluent, fraction VI	76.8	3.8	-
Effluent, fraction VII	88.2	4.0	-
Column feed (raw wastewater)		5.3	2,510

- = not analyzed

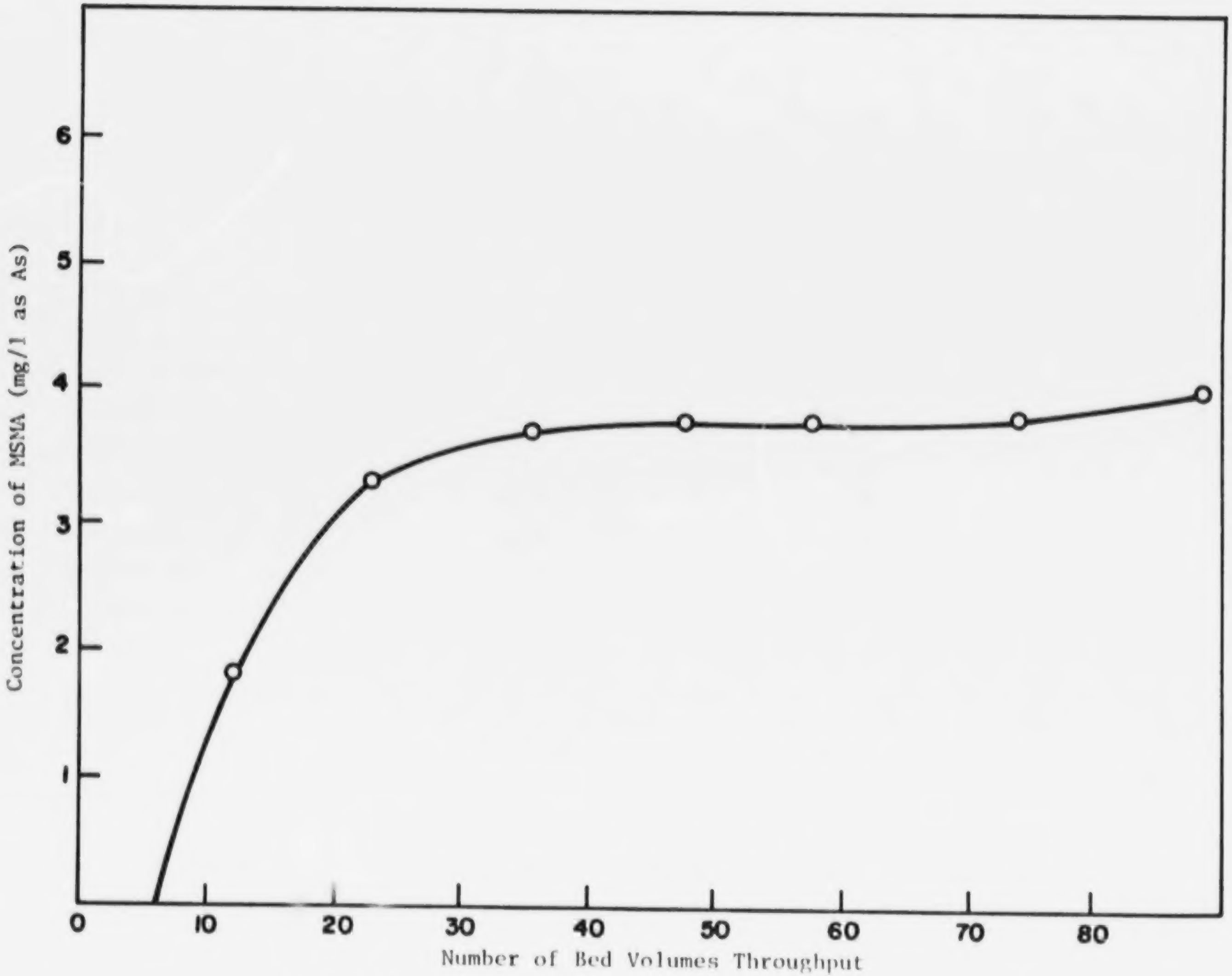


Figure 16. Carbon column treatment of MSMA.

wastewater unless no less costly alternative is available. Since the untreated wastewater has a total arsenic concentration of 22 mg/l, the MSMA (arsenic equivalence) represents only about 25% of the total arsenic. Thus, the MSMA may not be the most important component to consider. In any further treatability studies, both MSMA and arsenic analyses should be performed on all samples. The raw wastewater also contains a large amount of methanol (~ 1,600-3,000 mg/l), which would give a theoretical oxygen demand of 2400-4500 mg/l. Examination of the COD data indicate that at a throughput of greater than 11 bedvolumes little or none of the oxygen-demanding organic content was removed during GAC treatment. This was to be expected since methanol absorbs very poorly on activated carbon (Hager, 1974; Shumaker, 1977).

To get a better estimate of the actual carbon requirement, further studies should be conducted to determine at just what point breakthrough of MSMA and/or COD occurs. In determining overall costs, it should also be noted that this wastewater, unlike most wastewaters, does not require preliminary treatment to remove suspended solids.

Tests with algae (Appendix M) indicated that the inhibitory effects of the GAC-treated wastewater were essentially the same as for the untreated wastewater, with no growth occuring at a 10% (v/v) wastewater concentration.

BIOLOGICAL TREATABILITY STUDIES

Four activated sludge pilot units were set up with domestic sewage feed. Of these, two were controls and two received sewage supplemented with the MSMA wastewater (10% vol/vol). After a 10-day period of acclimation samples of influent and effluent from each unit were taken and analyzed for MSMA. Direct analysis by ion chromatography was not possible for these samples for two reasons: (1) the 10-fold dilution placed the final concentration at or below the limit of detection and (2) the sewage contained such high anion concentrations that simple concentration steps were not effective. As described in the methods section, pretreatment of the activated sludge wastewater samples by chloride removal made it possible to measure the MSMA. No interferences were noted in the MSMA wastewater alone.

Results of the analyses of the influents and effluents of the activated sludge units are given in Table 24. Concentration of MSMA in the effluent

Table 24. DETERMINATION OF EFFECTIVENESS OF ACTIVATED SLUDGE TREATMENT OF MSMA WASTEWATER

Sample	MSMA mg/l as As	% of Influent Value
I. Influents and Effluents		
10% MSMA Wastewater - Influent	0.27	--
- Effluent, Unit 1	0.29	109
- Effluent, Unit 2	0.29	109
Domestic Sewage Control - Effluent, Unit 1	Not detectable (<0.03)	--
Effluent, Unit 2	Not detectable (<0.03)	--
II. Sludges		
10% MSMA Wastewater, Unit 1	0.53	
Unit 2	0.53	

82

of the test units was comparable to that in the influent, giving evidence that activated sludge treatment was ineffective for its removal. As shown by the analytical results, the influent concentration was also considerably lower than would be expected in a 10% dilution of the wastewater (2.2 mg/l expected, 0.27 mg/l actually detected). This anomaly may result from either losses in the analytical workup, or, more likely, from removal of some of the soluble MSMA by sorption in the primary settling of the sewage/MSMA wastewater mixture. While such removal by sorption may occur, it must be noted that settling per se has not been considered a reliable method for removing asenic, since longterm experience of the manufacturer indicates no reduction of arsenic across the primary settling portion of the plant's wastewater treatment system.

Performance and operating characteristics of the units are shown in Tables 25 and 26 and in Figures 17 and 18. Despite the higher influent COD to the test units, the units performed about as well as the controls in terms of COD removal. Dissolved oxygen (DO) levels remained well above requirements, and pH in the test units was similar to that of the controls. Variability of effluent COD and SS values was to some extent due to operational problems with feed to the units.

Although COD reduction in the test units was reasonably good, ineffectiveness of AS for removal of MSMA and arsenic precludes recommending activated sludge alone as a satisfactory control technology. Removal of these components prior to activated sludge treatment would be desirable.

Only a relatively small amount of effluent was available for toxicity testing with fathead minnows since the raw wastewater was not very toxic. Replicate screening tests (6 fish total) were conducted on undiluted effluents from the test units and no deaths occurred in 96 hours.

Table 25. OPERATING CHARACTERISTICS OF BENCH SCALE ACTIVATED SLUDGE UNITS - MSMA WASTEWATER SERIES

		UNITS			
		Control		10% MSMA Wastewater	
Parameters	Day	I	II	I	II
DO, mg/1	1	5.7	5.8	6.9	7.4
	9	7.2	7.3	5.8	6.2
	15	7.1	7.1	5.3	6.5
pH	1	7.4	5.9	5.9	7.3
	8	5.6	5.7	6.7	6.6
	16	6.8	6.1	6.0	6.3
MLSS, ml/10 ml	1	0.4	0.5	0.45	0.25
	9	0.4	0.2	0.5	0.25
	15	0.1	0.15	0.5	0.25
	17	0.05	0.05	0.5	0.25

Table 26. PERFORMANCE CHARACTERISTICS OF BENCH SCALE ACTIVATED SLUDGE UNITS, MSMA WASTEWATER SERIES

		Control Units				Units fed 10% MSMA wastewater			
Parameter	Day	Influent	Effluent I	Effluent II	Ave % removal	Influent	Effluent I	Effluent II	Ave % removal
COD, mg/1	1-6	265				330			
	2		35	31	87		86	106	71
	4		32	32	87		36	80	82
	7-14	120				440			
	7		28	24	78		63	75	84
	9		14	79	61		18	50	92
	11		238	35	+		166	110	67
	14		106	40	40		60	106	81
	15-17	183				210			
	16		32	44	79		40	60	76
Effluent Suspended Solids mg/1	2		24	-			17	52	
	4		4	6			10	40	
	7		72	6			3	22	
	11		195	5*			77	39	

*Sludge was lost into the effluent. The effluent was allowed to settle, SS was determined on the supernatant, and the sludge was returned to the unit.

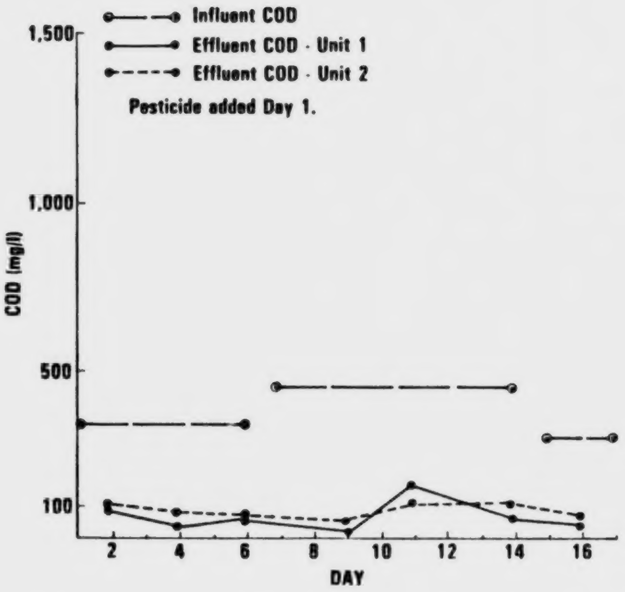


Figure 17. Influent and effluent COD for activated sludge units fed primary settled wastewater with 10% MSMA.

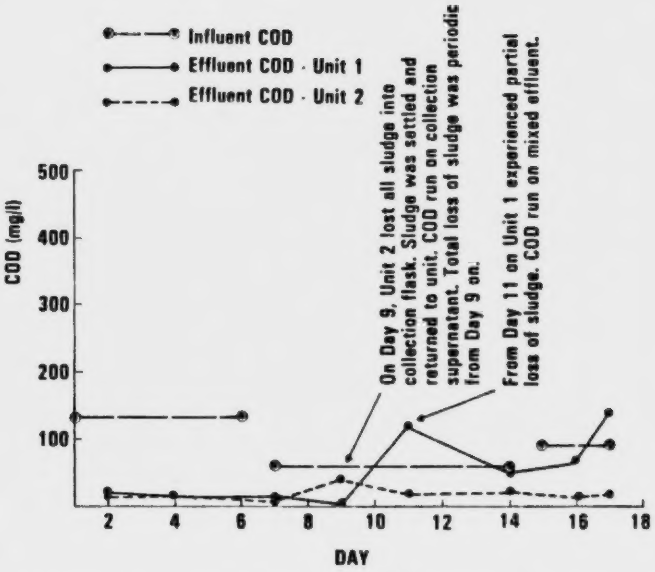


Figure 18. Influent and effluent COD for control activated sludge units fed primary settled wastewater alone.

SECTION 7

MANEB WASTEWATER TREATABILITY STUDIES

GENERAL BACKGROUND INFORMATION

Pesticide: Maneb CAS No.: 000301031

MEB; MnEBD, Manzate^{TM}; Dithane^{TM} M-22; Maneba^{R}; Manebgan^{R}; Manesan^{R}; Sopranebe^{R}, Trimangol^{R}; Vancide^{R}, Tersan LSR

Structure

Maneb is the general name for a class of formulations based on manganese ethylenebisdithiocarbamate. The different formulations vary considerably and may be toxicologically distinct from one another. Approximate formula (actually a polymer)

$$[S\text{-}SC\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CS\text{-}S]_x Mn_y$$

Manganous ethylene-1,2-bis-dithiocarbamate; [ethylenebis(dithiocarbamato)] manganese

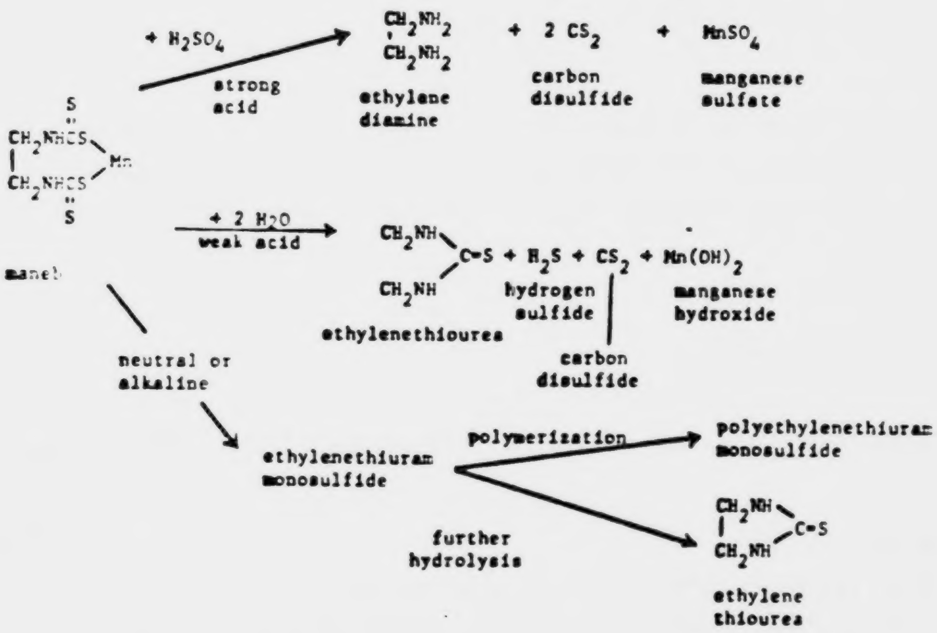
Chemical Category

Ethylenebisdithiocarbamate (EBDC)--Others in this class include ferbam, zineb, nabam, thiram, and ziram. Ethylene bisdithiocarbamates are also widely used as slimicides in the paper industry and are used in rubber processing.

Properties

MW 265.3--Decomposes before melting. Yellow crystalline solid. Stable to storage in dry air but decomposes in the presence of moisture to give carbon disulfide (CS_2) and ethylene thiourea (ETU). Maneb is insoluble in organic solvents. The apparent aqueous solubility of maneb determined in this study was 40 mg/l. Apparent maneb concentration is defined in terms of CS_2 generated by the sample under the conditions of maneb analysis (Appendix 6). The compounds determined included maneb and other compounds generating CS_2 (e.g., ethylene thiuram disulfide or monosulfide). The solubility was determined on aqueous filtrates which had been equilibrated with excess maneb at room temperature. pH and ionic strength will of course influence the value determined.

Hydrolysis reactions of maneb are complex and may occur under acid, alkaline, or neutral conditions, according to Shih and Dal Porto (1975):


+ H_2SO_4
strong acid
CH_2NH_2 / CH_2NH_2
ethylene diamine
+ 2 CS_2
carbon disulfide
+ $MnSO_4$
manganese sulfate
maneb
+ 2 H_2O
weak acid
ethylenethiourea
+ H_2S
hydrogen sulfide
+ CS_2
carbon disulfide
+ $Mn(OH)_2$
manganese hydroxide
neutral or alkaline
ethylenethiuram monosulfide
polymerization
polyethylenethiuram monosulfide
further hydrolysis
ethylene thiourea

Shih and Dal Porto (1975) also note that, in addition to the above reactions, under neutral or alkaline conditions formation of ethylene diisothiocyanate and ethylene diamine may occur. CS_2 evolution accompanies both alkaline hydrolysis and hydrolysis under strong acid conditions. Under some conditions chemical hydrolysis may produce ETU, as indicated in the diagram above. Chemical oxidation may likewise product ethylene-thiuram monosulfide which hydrolyses to ETU. For these reasons, these authors recommend disposal of commercial maneb preparations by burial or incineration, rather than by chemical treatment. However, for the more dilute pesticide manufacturing wastewaters, one cannot rule out the possible usefulness of hydrolysis under controlled conditions.

ETU is water-soluble [2 g/100 ml at 30°C (Merck Index, 1976)] and stable to sunlight, but presence of added photosensitizers (such as acetone or riboflavin) causes rapid photolysis; agricultural field waters taken from locations of dithiocarbamate application catalyzed ETU photodecomposition (Crosby, 1976).

Intended Use

Maneb is a fungicide for control of foliar fungal blights. It is recommended for prevention of early and late blight on tomatoes and potatoes, and can be combined with other fungicides for persistent fungal strains. EBDC fungicides are used in control of over 400 fungus diseases for protection of over 70 crops.

Mode of Action

Unknown.

Manufacturing Information - Introduced 1950

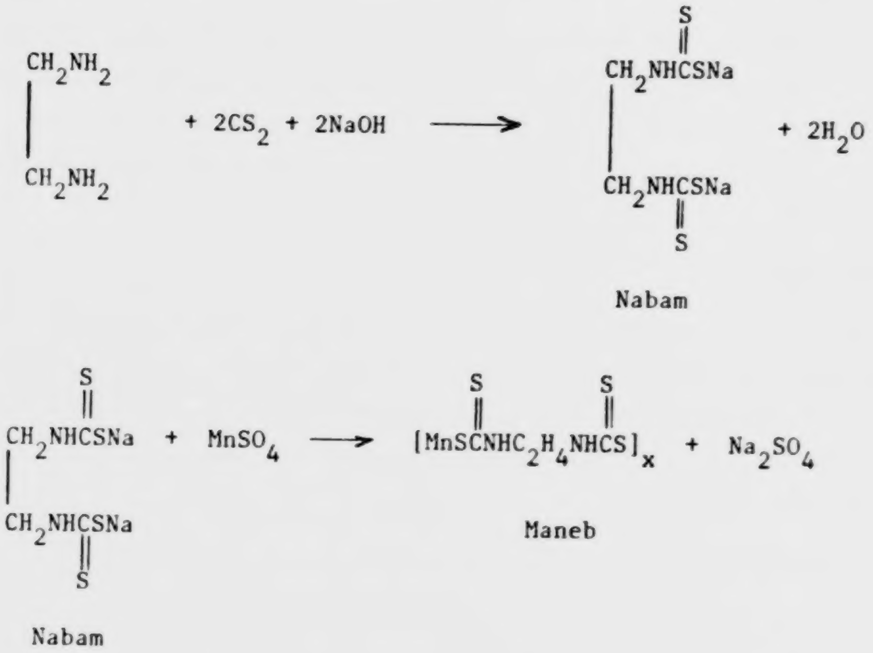
Estimated Amount Produced Annually: 5.4×10^3 metric tons in 1974 (Archer *et al*., 1978)

Manufacturers	Locations
DuPont	La Porte, TX
Rohm & Haas	Philadelphia, PA

Manufacturing Process

The processes described here are generalized and are not necessarily identical to those in operation at the plants sampled. According to the National Research Council (NRC, 1977) dithiocarbamates can be synthesized by reacting a suitable amine, such as dimethylamine or ethylenediamine, with CS_2 under alkaline conditions to yield the alkaline salt of the alkyl dithiocarbamic acid. These water-soluble salts can then be reacted with aqueous solutions of salts of zinc, manganese, and iron to form precipitates of the corresponding highly insoluble metallosalts. Alternatively, the metallosalts can be produced by reacting metal oxides with the appropriate amine and CS_2.

Sittig (1977) describes the reaction chemistry as follows:


CH_2NH_2
CH_2NH_2
$+ 2CS_2 + 2NaOH$
$CH_2NHCSNa$
$CH_2NHCSNa$
S
S
$+ 2H_2O$
Nabam
$CH_2NHCSNa$
$CH_2NHCSNa$
S
S
$+ MnSO_4$
$[MnSCNHC_2H_4NHCS]_x$
$+ Na_2SO_4$
Maneb
Nabam

Alternatively, maneb can be produced by reacting ethylenediamine with sodium hydroxide solutions and CS_2 to form the disodium ethylenebisdithiocarbamate, which is then reacted with manganous chloride to form the fungicide (Sittig, 1977). The major raw waste load from the maneb manufacturing process is the wastewater remaining after the precipitate is removed.

As summarized by Sittig (1977), air, liquid, and solid waste problems may occur. The liquid waste stream contains about 9 lb. of salts for each 13 lb. of maneb produced, these salts being primarily sodium sulfate with some manganese sulfate.

Health and Ecological Effects: Maneb

Mammalian Toxicity--

Toxicity rated as low:

Rat, oral LD_{50}: 6750 mg/kg (Fairchild, 1977)

Rat, inhalation, LC_{50}: 3000 mg/kg (Fairchild, 1977)

Recommended allowable daily intake, human: 0.005 mg/kg/day (NRC, 1977)

In animal metabolism studies with ^{14}C-maneb, about 55% was excreted as the metabolites ethylenediamine, ethylene-bis-thiuram monosulfide (ETM) and ETU, these metabolites associated mainly with the feces; no evidence for accumulation in tissues was found (NRC, 1977).

Aquatic Toxicity--

Aquatic toxicity rating, TLm, 96 hr.: 10-1 ppm (Fairchild, 1977).

Toxicity to fish, 96 hr TLm: 0.1-1.0 mg/l (Kemp *et al*., 1973).

Mutagenic Potential--

In vitro mutagenesis tests:

Ames test, only weakly mutagenic; *E. coli* B Y Vr-B strain, induced 5-fold increases in streptomycin resistant mutants (Warren *et al*., 1976).

Health and Ecological Effects: ETU

NRC (1977) notes that "the occurrence of ethylenethiourea (ETU) as a major decomposition product (of maneb)...presents a potential hazard since it is goitrogenic in laboratory animals and may produce thyroid carcinoma."

Rat, oral, 10 mg/kg/day: teratogenic (Khera, 1973)

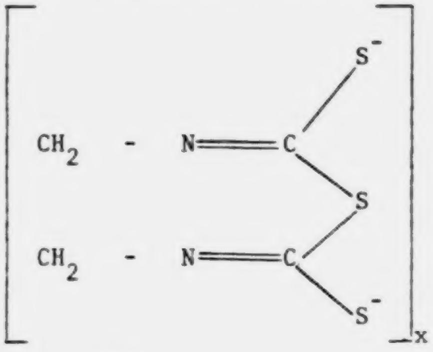
Weakly mutagenic to mammals (NRC, 1977); mutagenic to *Salmonella typhimurium* his G46 (Shirasu *et al*., 1977).

Produces hepatomas in mice (NRC, 1977)

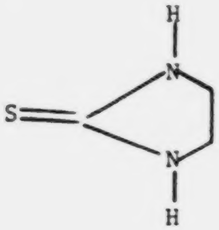
In summarizing their review of ETU the National Research Council has recommended "that very strict criteria be applied when limits for ETU in drinking water are established" (NRC, 1977). Weisburger (1977) recommends that "in view of the carcinogenicity of ethylenethiourea in two animal species, human exposure should be avoided." It should be stressed, however, that the validity of animal studies with ETU has been questioned and that additional animal studies with EDBC's are in progress (Gower and Gordon, 1979). For a recent review of the health effects of ETU see Gregory, 1978.

Potential Biodegradation Products

Packer (1975) indicates that biodegradation of maneb probably proceeds by first, a scission of MnS to form ethylene thiuram monosulfide polymer,



followed by loss of CS_2 to form ETU:



Current Waste Disposal Practice

Plant A	Treatment of raw wastewater with sodium hydroxide to remove manganese; precipitation of the insoluble $Mn(OH)_2$. Treatment of remaining wastewater by chemical oxidation, pH adjustment, and activated sludge. Wastes from the other products are treated in the same activated sludge unit, so efficiency of the maneb waste treatment alone cannot be calculated. The plant achieves an average of >99% BOD reduction and 70% COD reduction, representing excellent performance by activated sludge.

This system was adopted by Plant A after tests with chemical oxidation, pH adjustment, temperature treatments, iron salt precipitation, and carbon adsorption indicated that chemical oxidation was the method of choice for reducing fish toxicity.

Plant B — Pretreatment with skimming, neutralization, before discharge to a publicly owned treatment plant. (Communication, Environmental Sciences & Engineering)

CHARACTERIZATION OF MANEB WASTEWATERS

Wastewaters from each manufacturer of maneb were collected on-site, transported to RTI packed in ice, and analyzed for maneb and other components as described previously. Results of the analyses are shown in Table 27. Both wastewaters had the appearance of orange juice in respect to color and turbidity. Dissolved, suspended and settleable solids contents were extremely high for both plants as would be expected based on the manufacturing process. The Plant B sample had considerably higher levels of dissolved solids, inorganic nitrogen, and total pesticide. For each plant soluble pesticide levels were similar (40-46 mg/l) and approximated the aqueous solubility, ~ 40 mg/l.

At Plant A, nine five-gallon grab samples of wastewater were collected over a 2-week time period. Analysis of the wastewaters from each date gave an indication of the great variability of the strength of this flow (Table 28), with the total "maneb" pesticide concentration ranging from less than 1.5 to nearly 1240 mg/l (including particulates). The majority of the values ranged from 100-400 mg/l. These stated concentrations of maneb included particulate maneb present in the sample as received. Before conducting the studies described below, each of the daily samples was mixed thoroughly and equal aliquots from each daily sample were composited. All full scale tests described below were run on this composited sample. The magnitude of the variation indicates that the wastewater may be difficult to treat biologically unless the effect of slugs can be moderated by load equalization prior to biological treatment or by treatment in a unit with long detention time, where the daily influent would represent only a small

Table 27. CHARACTERIZATION OF MANEB WASTEWATERS

	Plant A		Plant B	
Parameter	Sample 1	Sample 2	Sample 1	Sample 2
pH	6.8	6.9		7.8
Cl^-, mg/l	640	770	990	840
Alkalinity, mg/l as $CaCO_3$	55.0	45.0	152	120
TKN, mg/l	880	740	6,100	3,660
NH_4-N, mg/l	560	640	930	3,580
NO_2-N+NO_3-N, mg/l	-	4.0		60
TP, mg/l		0.3	0.01	0.1
COD, mg/l	8,800	4,140	2,400	2,000
Sol. COD, mg/l			1,980	
Suspended solids, mg/l		1,990	1.0	1,600
Total solids, mg/l		24,800		102,000
Total dissolved solids, mg/l		22,800		100,400
Settleable solids, ml/l		74		9.5

TABLE 28. STUDY OF VARIATION IN MANEB MANUFACTURING WASTEWATER

Date	Concentration of Maneb and Related Compounds (ppm)
5/30	1240
5/31	400
6/1	110
6/2	360
6/7	130
6/8	1.40
6/9	140
6/13	130
6/13	120

portion of the total volume. Such variation should have less effect on performance of physical-chemical treatment systems. However, in GAC column systems the daily variation may complicate reliable prediction of carbon requirements and breakthrough time. Frequent monitoring of the effluent would be necessary.

Plant B wastewater samples represented a mixture of wastes from the straight line filter and from the scrubber. The straight line filter is the largest source of effluent from the maneb production process. The scrubber contributes the next largest flow. In actual practice these waste streams enter the sewer with much additional wastewater from vacuum jets, tote-bin washout, and wastewater from production of other pesticides. This combined wastewater is then subjected to settling prior to discharge to the main plant sewer. The Plant B wastewater sample from the scrubber and filter was collected at a point prior to any mixture with other waste streams, and thus represents a waste stream with maximum maneb content.

Toxicity tests were conducted on fathead minnows with both wastewaters and with commercial maneb. Screening tests with commercial maneb indicated the 96 hr LC_{50} to be between 0.1-1.0 mg/l (Bioassay data are presented in Appendix N). Screening tests with Plant A wastewater showed the 96 hr LC_{50} for fish to be between 0.1 and 1% for both filtered and unfiltered samples. The 96 hr LC_{50} of unfiltered Plant B wastewaters was between 0.01 and 0.1% (v/v), while filtered wastewater was less toxic with a 96 hr LC_{50} between 0.1 and 1%. A definitive fish bioassay with unfiltered Plant B wastewater gave a 96 hr LC_{50} between 0.056 and 0.1% (v/v).

Full scale fish bioassay of unfiltered Plant A wastewaters (Sample 2) showed a 96 hr LC_{50} of approximately 1.8 ml/l or 0.18%. Filtered Plant A wastewater was much less toxic with a 96 hr LC_{50} > 32 ml/l or 3.2%. Several factors could account for the higher toxicity of unfiltered Plant A wastewater. Solid material probably redissolves to the point of saturation subsequent to dilution and thus is made more available to fish. It was also noted that fish tended to "mouth" pieces of solid material, thus increasing exposure to possibly toxic material.

Full scale fish bioassay of Plant B wastewater (Sample 2) resulted in the same pattern as Plant A wastewater. The 96 hr LC_{50} of unfiltered Plant

B wastewater was approximately 0.18 ml/l (0.018%) while filtered wastewater showed a 96 hr LC_{50} of approximately 3.2 ml/l.

Unfiltered Plant B wastewater was consistently more toxic than unfiltered Plant A wastewater. Zinc was reported by plant personnel to be present in the Plant B wastewater due to plant production of both Mn and Zn forms of the fungicide. In soft water 96 hr LC_{50} values for zinc for fish are in the vicinity of 2-4 mg/l (McKee and Wolf, 1963). If present, zinc could be partially responsible for the greater toxicity of Plant B wastewaters as compared to Plant A wastewater.

In screening tests with algae wastewaters from both Plant A and Plant B were inhibitory to algal growth at concentrations of 0.1% and above. Since these wastewaters were filter-sterilized prior to addition to algal assays, the soluble fractions of each waste appear equally toxic to algal growth. Further tests with Plant B wastewater, using a narrow range of test concentrations, indicated that the 14-day EC_{50} was 0.06-0.1%.

In bacterial spot tests all undiluted maneb manufacturing wastewaters produced marked zones of inhibition (Appendix O). This indicates that the undiluted wastewater would be apt to interfere with activity of the organisms present in sewage and possibly interfere with biological treatment systems.

ACTIVATED CARBON TREATABILITY STUDIES

Maneb manufacturing wastewaters were subjected to activated carbon treatment in liquid adsorption isotherm and GAC column studies. Since, as noted previously, aqueous preparations of maneb have a strong tendency to undergo decomposition to the breakdown products ethylene dithiocarbamate monosulfide (ETM), ethylene dithiocarbamate disulfide (ETD), and ethylene thiourea (ETU), even in the dark in cold storage (Czeglédi-Jankó, 1967), and since ETU is considered a more hazardous compound than is maneb (NRC, 1977), concentrations of these breakdown products, as well as maneb, were determined.

Adsorption Isotherm Studies

Activated carbon isotherm studies with the wastewaters (Tables 29 and 30, Figure 19) indicated that maneb could be removed to low levels by

Table 29. LIQUID ADSORPTION ISOTHERMS FOR TWO MANEB MANUFACTURING WASTEWATERS

Carbon: Calgon Filtrasorb 400

M **Wt. of Carbon, g/100 ml of Solution**	**C** **Residual Pesticide, mg/l**	X Pesticide Adsorbed mg/l	X/M Pesticide Adsorbed Per Unit Weight g/g
Plant A*			
0	1.2	-	
0.04	0.43	0.77	0.0019
0.08	0.25	0.95	0.0012
0.16	0.19	1.01	0.0006
2.0	0.05	1.15	0.00006
Plant B			
0	19.1	-	
0.04	5.9	13.2	0.033
0.08	3.8	15.3	0.019
0.16	0.74	18.36	0.011
2.0	0.30	18.8	0.009

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*Initial concentration of the maneb in the sample tested was very low

Table 30. LIQUID ADSORPTION ISOTHERM FOR PLANT B MANUFACTURING WASTEWATER

Carbon: Calgon Filtrasorb 400

M Wt. of Carbon, g/100 ml of Solution	C Residual Pesticide, mg/1	X Pesticide Adsorbed, mg/1	X/M Pesticide Adsorbed Per Unit Weight, g/g	X/M at C_o
0	30.10	--	--	
0.04	1.14	28.96	.0724	
0.08	0.48	29.62	.0370	
0.16	0.25	29.85	.0186	12.5
2.0	not detectable*	~30.10		

*< 0.15 mg/1

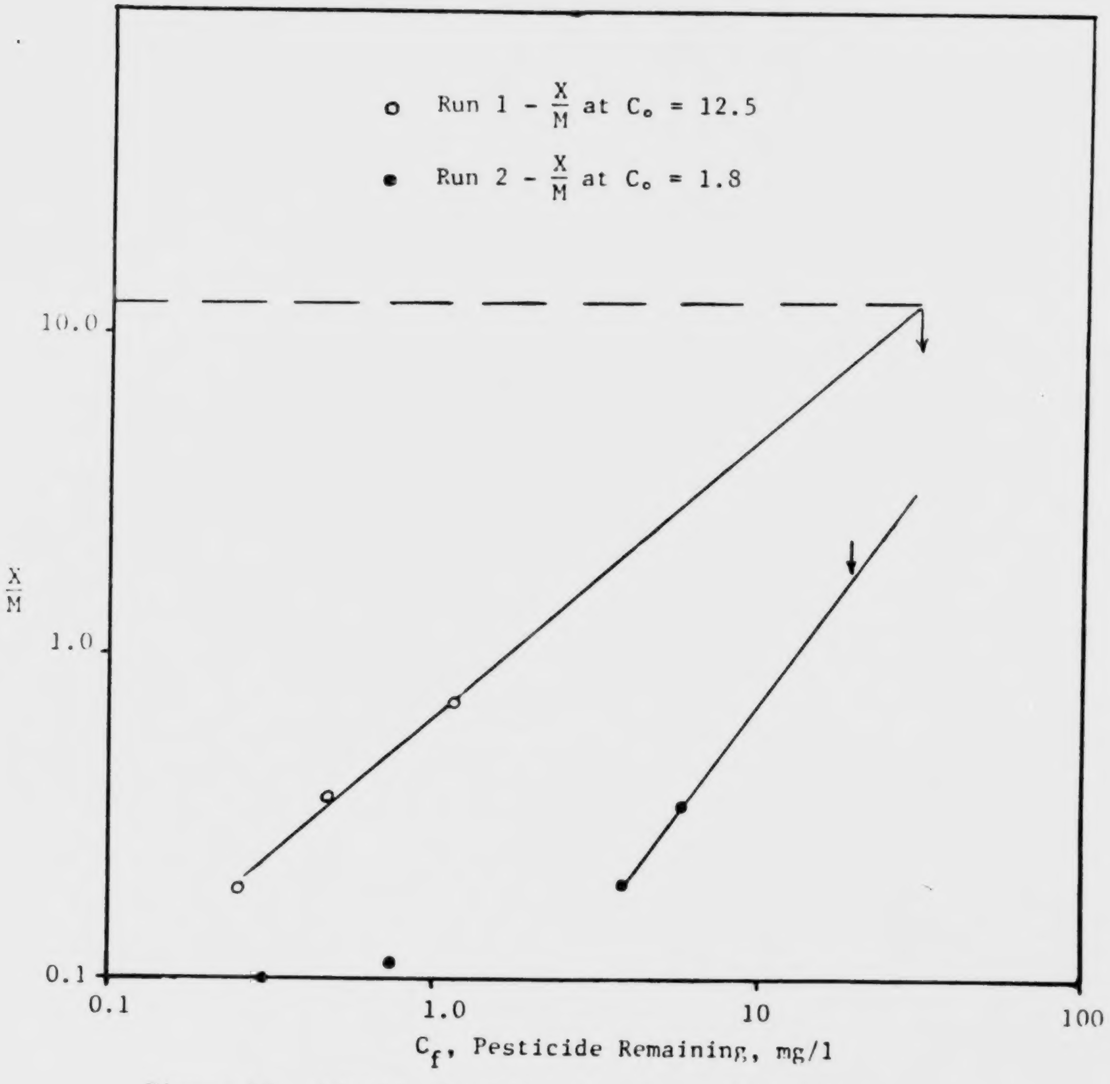

Figure 19. Liquid adsorption isotherms for Plant B manufacturing wastewaters.

Table 31. ADSORPTION ISOTHERM STUDIES OF ABILITY OF ACTIVATED CARBON TO REMOVE ETU FROM PLANT A WASTEWATERS

Sample	Carbon	Amount of Carbon g/100 ml	ETU in solution in filtrate, mg/l
Plant A Wastewater	None	0	31 ± 7
	Filtrasorb 400	0.08	29
		0.16	23
		2.0	<6
	Nuchar WV-L	0.16	38
		2.0	<13
	Nuchar SA	0.16	34
		2.0	<14
	Nuchar WV-G	0.16	47
		2.0	<14
	UC-LCL	0.16	25

activated carbon. The results of isotherm studies with ETU indicated possible removal of ETU by carbon treatment. This option was pursued further with GAC column studies. Filtrates from the carbon isotherm studies with Plant B wastewater were subjected to thin layer chromatography (Czeglédi-Jankó, 1967) for maneb breakdown products. Figure 20 shows the chromatograms obtained by scanning densitometry. In this figure the area where ETU would appear is deleted since ETU concentrations were so high that the detection system was saturated. The 10 minute exposure to iodine vapor was insufficient to develop full color in the center of the ETU spot ("concentration reversal"); however this exposure gave best visualization of the other breakdown products. The same plate was exposed to iodine vapor for an additional 30 min and rephotographed and rescanned (Figures 21 and 22). Even at this much longer exposure there was still some concentration reversal at the higher ETU concentrations which indicated insufficient exposure to and complexing with the iodine vapor. It was possible under these conditions to estimate the amount of ETU originally present in this wastewater sample at 300 to 600 mg/ℓ. Treatment with 2.0 g of activated carbon/100 ml of filtered wastewater removed 90 to 95% of the ETU.

GAC Column Studies

Plant B wastewater was subjected to GAC treatment. A column 2.5 cm in diameter was filled to a depth of 1.2 m with 360 g of carbon (Calgon Filtrasorb 400). The filtered wastewater was pumped onto the column to give a flow rate of 12.5 ml/min (0.607 gpm/ft^2). Approximately one bed volume (650 ml) was discarded before fraction collection was initiated. The data are given in Table 33. No maneb or maneb decomposition products were detected in any fractions.

Since no breakthrough of maneb was observed the procedure was repeated with a smaller column. A 2.7 cm i.d. column was filled to 15 cm with 58.8 g of activated carbon. Filtered maneb wastewater was pumped through the column at 12.5 ml/min (0.529 gpm/ft^2). One bed volume (85 ml) was discarded before collecting effluent fractions. The data are given in Tables 34 and 35. Simple filtration removed suspended solids and a substantial portion of the COD (~79%), indicating that efficient settling or filtration processes

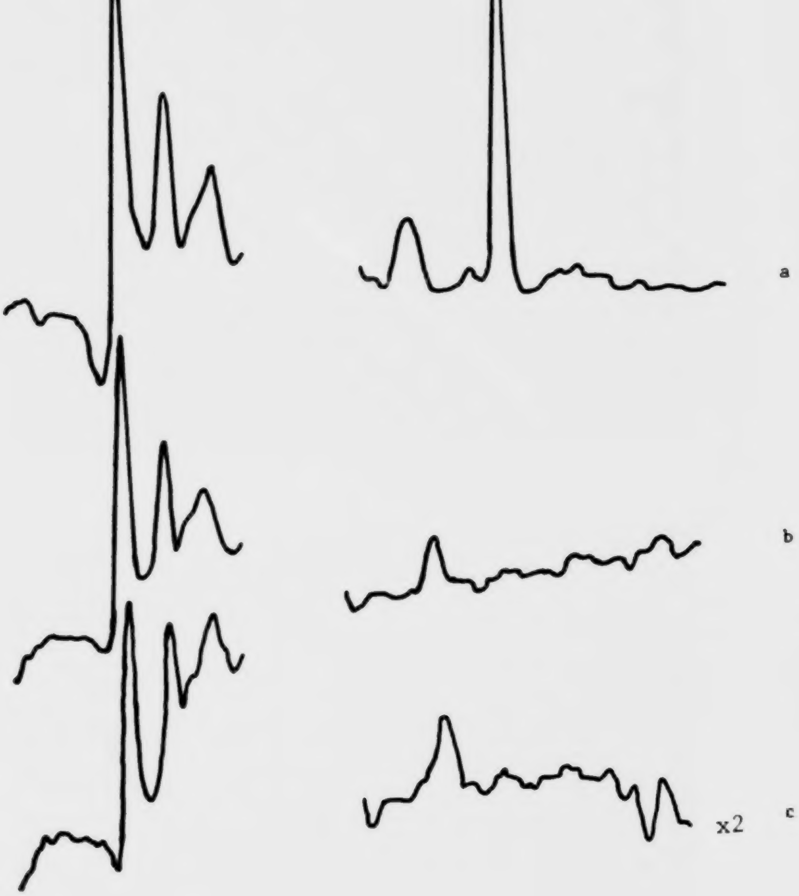

Figure 20. Thin-layer chromatogram of Plant B wastewater and filtrates of carbon isotherm determination. (a) 10 µl untreated wastewater; (b) 50 µl treated with 0.04 g carbon/100 ml wastewater; (c) 50 µl wastewater treated with 0.08 g carbon/100 ml. Absorbance sensitivity is twice that of a and b.

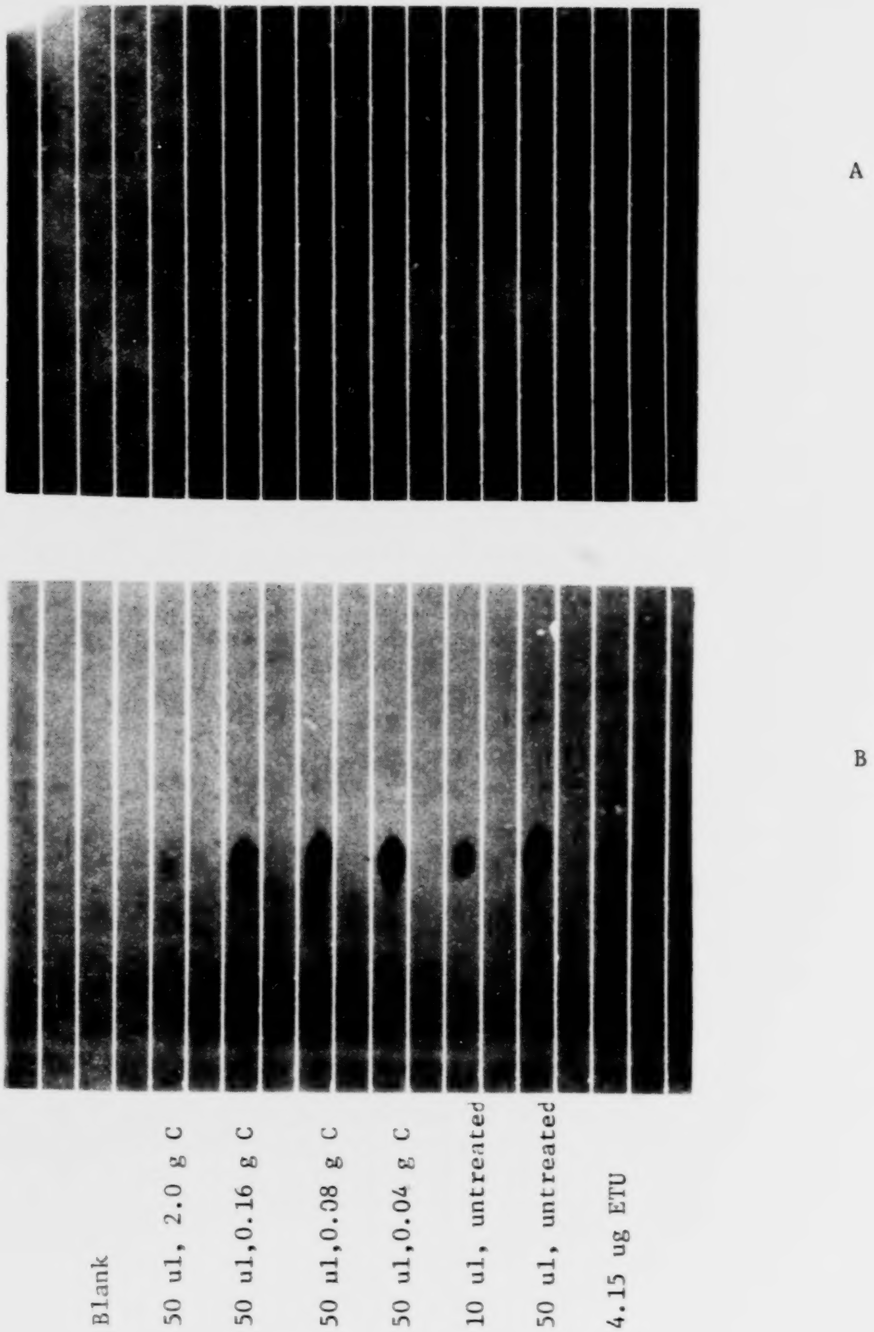
A
B
Blank
50 ul, 2.0 g C
50 ul,0.16 g C
50 ul,0.08 g C
50 ul,0.04 g C
10 ul, untreated
50 ul, untreated
4.15 ug ETU

Figure 21. Thin-layer chromatograms of carbon isotherm filtrates - A. 10 min iodine exposure. B. 30 min iodine exposure. Plant B wastewater.

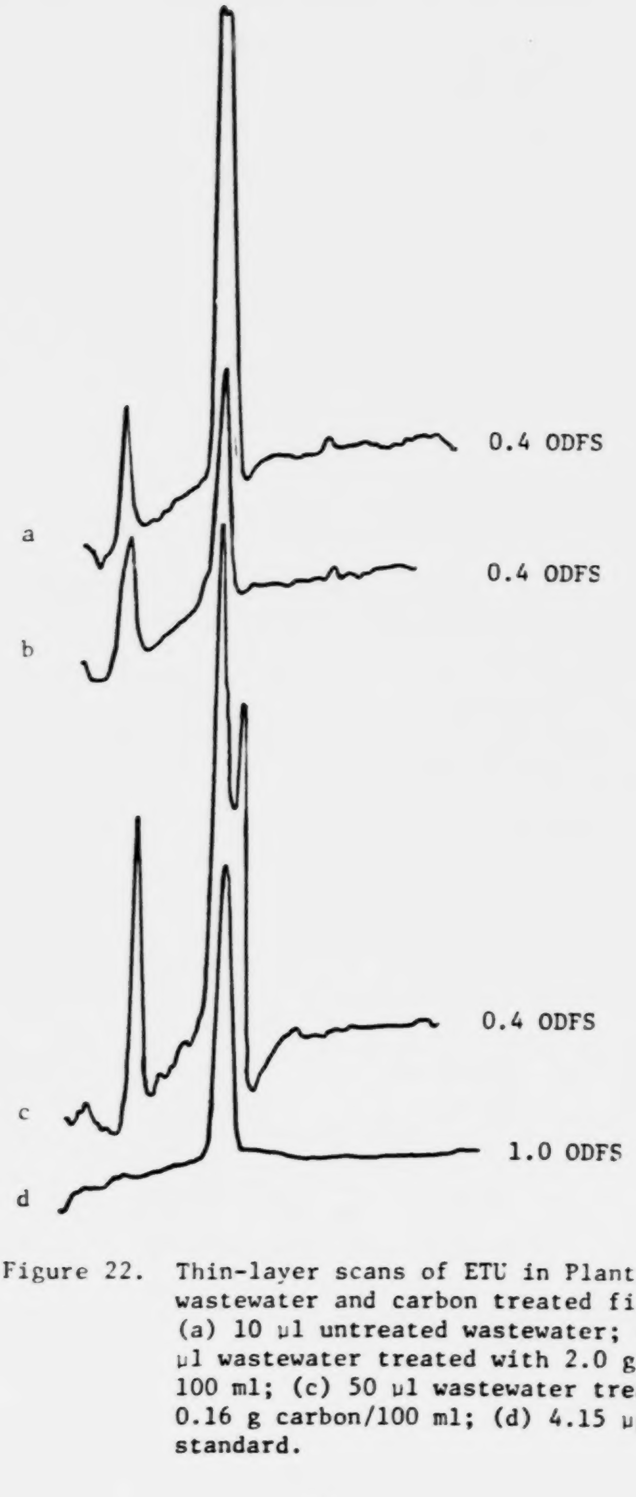

Figure 22. Thin-layer scans of ETU in Plant B wastewater and carbon treated filtrate: (a) 10 μl untreated wastewater; (b) 50 μl wastewater treated with 2.0 g carbon/100 ml; (c) 50 μl wastewater treated with 0.16 g carbon/100 ml; (d) 4.15 μg ETU standard.

Table 32. EFFECT OF GAC COLUMN TREATMENT OF PLANT A WASTEWATER

Fraction No.	Cumulative No. of Bed Volumes	Maneb mg/l	ETU mg/l
I	11.0	< 0.15	< 1.0
II	22.0	< 0.15	< 1.0
III	33.0	< 0.15	< 1.0
IV	44.0	< 0.15	1.1
V	55.0	< 0.15	4.4
VI	66.0	< 0.15	4.2
VII	77.0	< 0.15	-
VIII	88.0	< 0.15	-

Table 33. EFFECTIVENESS OF GAC TREATMENT OF PLANT B WASTEWATER-RUN I (1.2 m column)

Column Effluent Fraction No.	Cumulative No. of Bed Volumes	Maneb Concentration, mg/l	Maneb Decomposition Products Present?
I	1.62	<0.15	No
II	3.24	<0.15	-
III	4.86	<0.15	No
IV	6.47	<0.15	-
V	12.46	<0.15	No
VI	14.08	<0.15	-
VII	15.70	<0.15	No
VIII	17.32	<0.15	No
IX	18.93	<0.15	-
X	20.55	<0.15	No
XI	21.80	<0.15	-

Table 34. EFFECTIVENESS OF GAC TREATMENT OF PLANT B WASTEWATER-RUN II (15 cm column)

Column Effluent Fraction No.	Cumulative No. of Bed Volumes	Maneb Concentration, mg/l
I	17.9	<0.1
II	29.4	<0.1
III	40.8	<0.1
IV	52.8	<0.1
V	64.2	<0.1
VI	75.7	<0.1
VII	87.2	<0.1

Table 35. EFFECTIVENESS OF FILTRATION AND GAC TREATMENT REDUCING COD OF PLANT B WASTEWATER

Sample	COD, mg/l	
	Replicate I	Replicate II
Unfiltered wastewater	7,500*	
Filtered, Whatman 2V (column feed)	1,600	1,600
GAC Treated, 1st Effluent fraction (Calgon Filtrasorb 400)	100	100

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*Due to the presence of fine solids in the Plant B wastewater, obtaining reproducible COD values was difficult. This value represents a "best estimate" of the COD concentration.

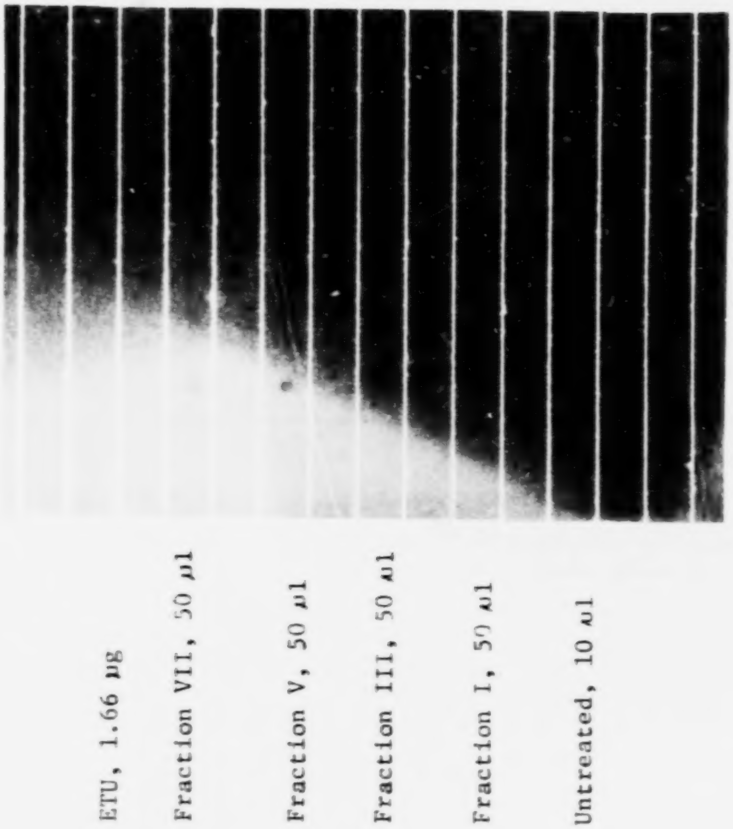

ETU, 1.66 µg
Fraction VII, 50 µl
Fraction V, 50 µl
Fraction III, 50 µl
Fraction I, 50 µl
Untreated, 10 µl

Figure 23. Thin-layer chromatogram of untreated and GAC-treated wastewater from Plant B.

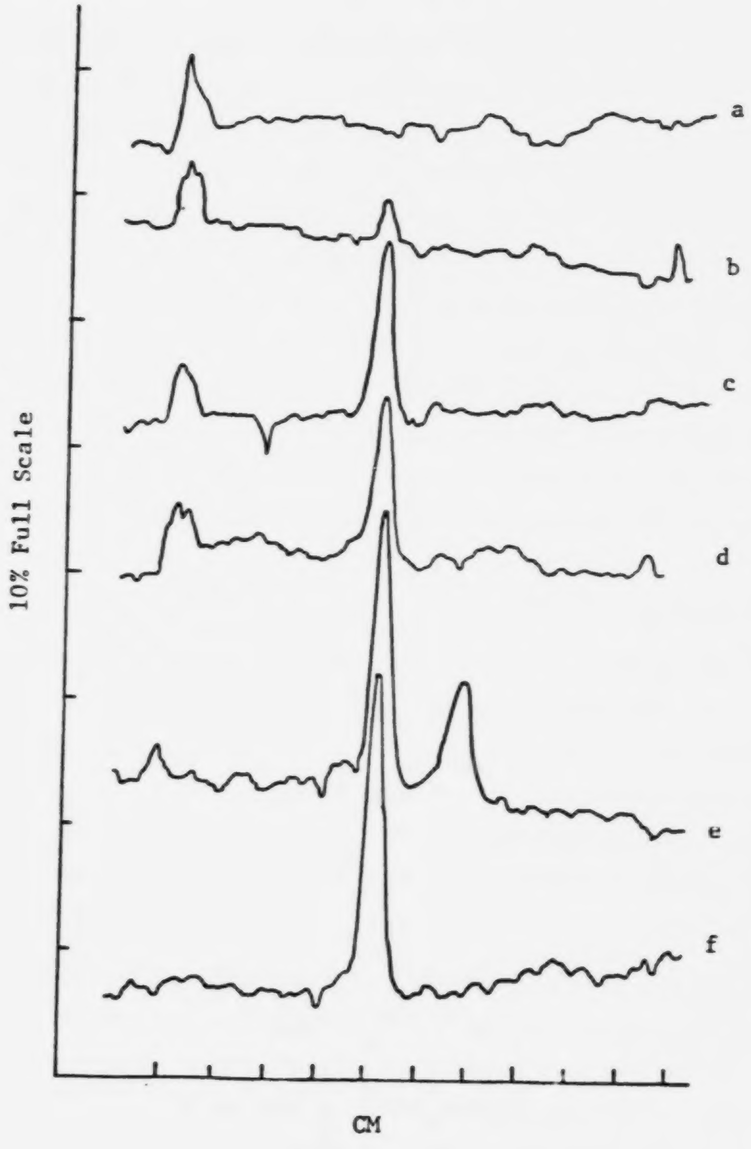


Figure 24. Thin-layer chromatograms of ETU and extracts of carbon column effluent in the treatment of Maneb wastewater. (a) 50 μℓ Fraction III (23-33 column volumes). (b) 50 μℓ Fraction IV (34-44 column volumes). (c) 50 μℓ Fraction V (45-55 column volumes). (d) 50 μℓ Fraction VI (56-66 column volumes). (e) 10 μℓ wastewater filtrate, untreated. (f) 0.41 μg ETU.

in themselves would effect an impressive degree of treatment. GAC treatment reduced COD to 100 mg/l, equivalent to removal of 94% of the COD in the column feed and >98% of the COD in the unfiltered wastewater.

All of the fractions were analyzed for maneb by the headspace method (Appendix F) and none was detected in any fraction (<0.15 ppm) (Table 34). This was despite the appearance of particulate at the top of the carbon column from the start of fraction IV. Analysis for breakdown products by tlc was performed on the odd numbered fractions. The results are shown in Figures 23 and 24 and plotted in Figure 25. Fractions I and III are free of any detectable breakdown products. Fraction V shows the presence of ETU at 20-40 ppm. By fraction VII the ETU concentration was approximately 20% (∿ 60-120 ppm) of the original untreated wastewater. Breakthrough for ETU occurred between 40.8 and 64.2 bed volumes (Figure 25). Another breakdown product (ETM) was observed in fraction VII (Figure 22). It is unclear whether the larger volume prior to ETM breakthrough is attributable to the lower concentration of this component in the wastewater or to less sensitivity of the analysis of ETM.

Based on results of carbon treatment of Plant B wastewater Plant A wastewater was subjected to short GAC column treatment, using a 2.7 cm i.d. column filled to 15 cm with 48.8 g of carbon. Filtered wastewater was pumped through the column at 12.5 ml/min (0.529 gpm/ft^2). One bed volume (85 ml) was discarded before collecting fractions. The data are shown in Table 32. Carbon required to reduce ETU to < 1.0 mg/l would be 107 lbs/1000 gallons.

Effect of GAC Column Treatment on Toxicity to Fish and Algae

Tests with untreated Plant A wastewater indicated the 96 hr LC_{50} to be 1.8 ml/l, while simple filtration reduced the toxicity to an LC_{50} of > 32 ml/l. Due to volume constraints it was not possible to run toxicity tests at dosages of GAC treated wastewater higher than 32 ml/l so it is not possible to determine if GAC treatment significantly affected toxicity; however, the LC_{50}, as expected, was > 32 ml/l. Untreated Plant B wastewater had an LC_{50} of ∿ 0.14-0.17 ml/l, which was increased to ∿ 3.2 ml/l by simple filtration and to > 3.2 ml/l by GAC treatment.

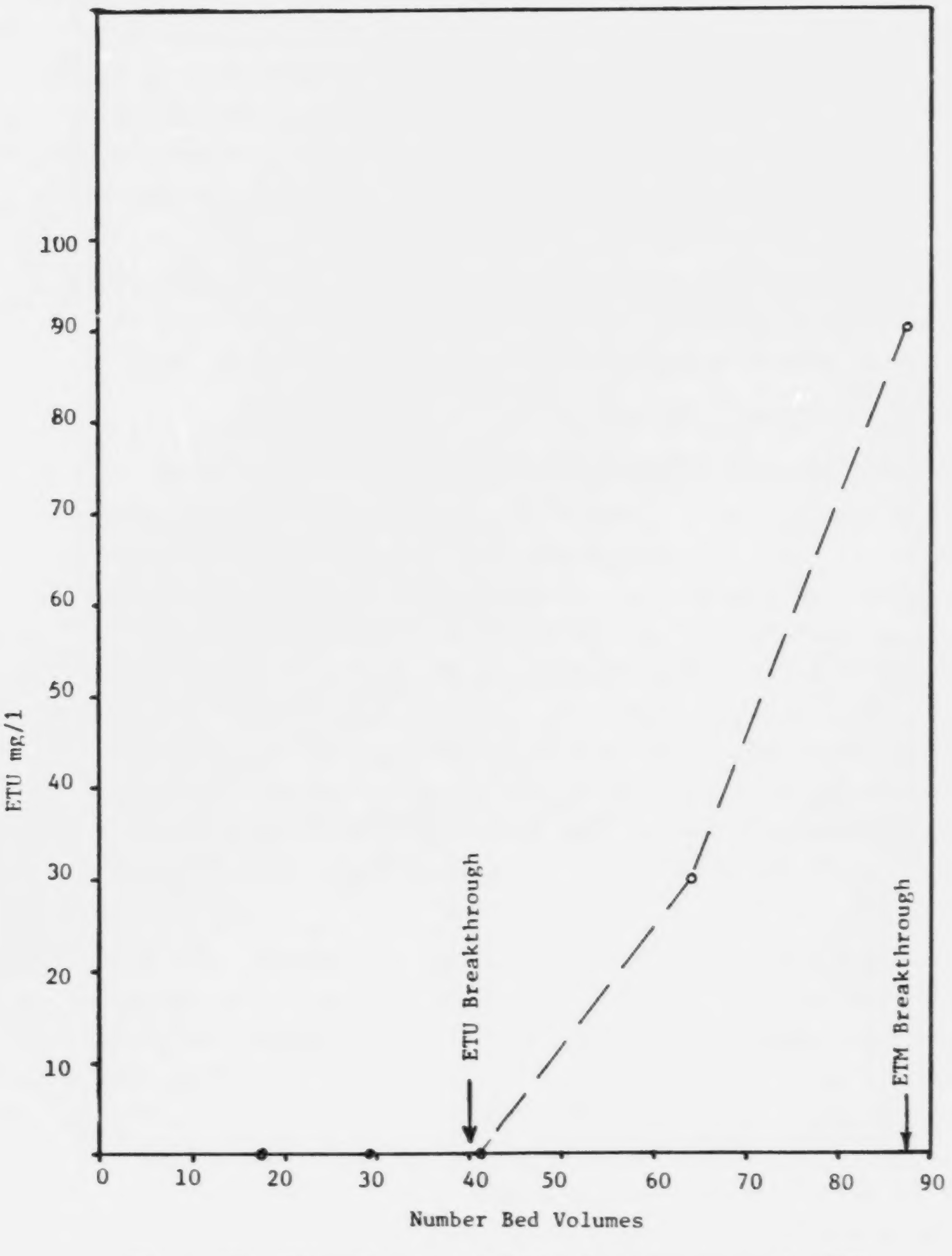


Figure 25. Effectiveness of GAC column treatment for ETU removal from Plant B wastewater.

In algal assay studies GAC treated wastewater from either plant inhibited growth at concentrations of 0.1% and concentrations less than 0.1% generally had little effect on growth. Since wastewater treated by simple filtration gave similar results, GAC treatment cannot be credited with significant removal of toxicity. The component(s) of the wastewater responsible for the algal toxicity, as well as the residual fish toxicity, is unknown.

It should be further noted that carbon treatment failed to eliminate toxicity to sewage flora (Appendix O), so that the maneb and its breakdown products were evidently not the components responsible for the toxicity.

BIOLOGICAL TREATABILITY STUDIES

Effect of Biological Treatment on Pesticide Removal

Maneb manufacturing wastewaters were diluted to 10% (v/v) with municipal sewage and fed to bench-scale activated sludge units. The wastewater mixtures were subjected to primary settling prior to AS treatment. Results taken after two weeks of operation are shown in Table 36. These results indicate that there was some reduction in the already low maneb concentration, but that there were appreciable concentrations of ETU in the effluents. Because of the oncogenic potential of ETU further investigations should be conducted to determine if these concentrations have an adverse health or ecological effect when biologically treated wastewaters are released to the environment. It should be noted that further treatment with GAC would eliminate the ETU.

Determinations of "maneb" (maneb and related compounds) were also made on the sludge from each set of units after termination of the experiment. Because of the nature of the sludge, which contained components which interfered with the analysis, these determinations cannot be considered to be very accurate. Results showed the "maneb" concentration to be 213 ± 70 mg/l in the control units, 895 ± 41 mg/l in those units with Plant A wastewater, and 940 ± 50 mg/l in the units with Plant B wastewater. The concentrations in the test units were over 4X that in the control units and in all cases were many times greater than in the effluents.

Table 36. MANEB AND ETU CONCENTRATIONS IN INFLUENTS AND EFFLUENTS FROM ACTIVATED SLUDGE UNITS

Type	Stream	Sample 1		Sample 2	
		Maneb and related cpds. mg/1	ETU mg/1	Maneb and related cpds. mg/1	ETU mg/1
Control (Municipal Sewage)	Influent	ND	-	ND	ND
	Effluent, Unit 1	ND	ND	ND	ND
	Effluent, Unit 2	ND		ND	-
Maneb, Wastewater A (10%, in municipal sewage)	Influent	2.1	-	1.25	52
	Effluent, Unit 1	0.67	60	0.61	34
	Effluent, Unit 2	0.49	26	0.52	22
Maneb, Wastewater B (10% in municipal sewage)	Influent	1.9		2.27	103
	Effluent, Unit 1	0.67	120	1.63	86
	Effluent, Unit 2	1.16	143	2.20	76

ND = not detectable (<0.1 mg/1)

Performance and operating characteristics of the units are shown in Tables 37-39 and in Figure 26. COD removals in the units showed some variation, but as is obvious from Table 37, performance of the units fed maneb wastewaters was consistently less than that of the control units, and the units fed Plant B wastewater consistently showed the poorest performance. Suspended solids levels in the effluents from the test units were generally greater than in the effluents from the control units, averaging about twice as high (Table 38). However, these levels are still in the range of values typical of effluents from well-operated biological treatment systems.

Examination of the operational data (Table 39) reveals difficulty in maintaining mixed liquor suspended solids (MLSS) levels in several units. Because of operational difficulties with the units it is not possible to determine if addition of pesticide wastewater was the primary cause of this loss. If so, it would portend a gradual loss of the activated sludge (and of the treatment efficiency) of the units.

The pH of mixed liquor in the aerators of the control units was consistently slightly lower than neutral (5.1-6.7), as would be expected if some degree of nitrification were taking place. The pH in the test units was consistently above neutral (7.6-7.9) and possibly indicates that nitrification was not occurring.

Further evidence of effects on nitrification is provided by the following data:

AS Unit	Influent NH_3, mg/l as N	Effluent NH_3, mg/l as N
Control	17	< 1
Test - Plant A	84	63
Test - Plant B	300	440

Thiourea compounds are well-known inhibitors of nitrification (see review in Thiman, 1963).

Algal assay tests were conducted on composited influents and effluents of the units receiving Plant A and Plant B wastewaters (Appendix 14). No growth occurred in the presence of 10% concentrations of Plant A influents

Table 37. PERFORMANCE CHARACTERISTICS OF BENCH-SCALE ACTIVATED SLUDGE UNITS, MANEB WASTEWATER SERIES - ABILITY OF UNITS TO REMOVE COD

Day	Control Units				Units fed Plant A Wastewater (10%)				Unit fed Plant B Wastewater (10%)			
	COD, mg/ℓ			COD removal, % (average of two units)	COD, mg/ℓ			COD removal, % (average of two units)	COD, mg/ℓ			COD removal, % (average of two units)
	Influent	Effluent			Influent	Effluent			Influent	Effluent		
		Unit I	Unit II			Unit I	Unit II			Unit I	Unit II	
15*	-	-	25	-	-	110	87	-	-	99	140	-
17	100	16	20	82	325	180	210	42	140	-	190	None
22**	-	47	78	-	-	204	244	-	-	210	275	-
25	110	32	17	78	368	164	172	55	340	216	224	35
28	150	34	-	73	400	140	150	64	310	180	190	40
30	90	35	35	61	300	150	160	48	235	200	260	0
32	150	36	28	80	320	162	160	50	225	214	230	32
35	140	32	60	67	260	170	146	39	-	160	230	-
36	80	32	60	42	240	170	150	33	242	190	190	21

*Pesticide wastewater was added to test Units on day 14.

**Some difficulty with air fed to units was experienced on day 22.

Table 38. PERFORMANCE CHARACTERISTICS OF BENCH-SCALE ACTIVATED SLUDGE UNITS, MANEB WASTEWATER SERIES--SUSPENDED SOLIDS LEVELS IN EFFLUENTS

Parameter	Day	Control Units		Units Fed Plant A Wastewater (10%)		Units Fed Plant B Wastewater (10%)	
		I	II	I	II	I	II
Effluent Suspended Solids, mg/1	21	30	30	70	80	30	50
	23	30	30	70	80	30	50
	25	20	-	50	60	60	40
	30	30	30	30	40	60	30
	32	30	30	50	50	60	60
	35	15	6	30	21	25	50
	36	3	4	45	26	25	40
Ave. Value, mg/1		22		50		44	
Range, mg/1		3-30		21-80		25-60	

Table 39. OPERATING CHARACTERISTICS OF BENCH SCALE ACTIVATED SLUDGE UNITS (MANEB WASTEWATER SERIES)

		Control Units		Units Fed Plant A Wastewater, 10%		Units Fed Plant B Wastewater, 10%	
Parameter	Day*	I	II	I	II	I	II
MLSS	1	0.35	0.21	0.31	0.27	0.32	0.36
(centrifuged,	2	0.30	0.19	0.28	0.20	0.30	0.30
ml/10 ml)	6	0.25	0.22	0.20	0.17	0.32	0.32
	7	0.30	0.20	0.20	0.19	0.30	0.30
	8	0.28	0.20	0.20	0.13	0.30	0.30
	9	0.20	0.18	0.18	0.12	0.30	0.30
	10	0.23	0.20	0.20	0.12	0.30	0.30
	13	0.25	0.18	0.20	0.12	0.30	0.28
	14	0.25	0.20	0.20	0.12	0.30	0.20
	17	0.30		0.20	0.12	0.30	0.17
	21	0.21	0.18	0.20	0.10	0.25	0.19
	22	0.25		0.17		0.25	0.12
	24	0.28	0.22	0.15	0.11	0.25	0.12
	27	0.25	0.21	0.15	0.10	0.25	0.10
	30	0.23	0.30	0.11	0.10	0.25	0.10
	32	0.25	0.21	0.11	0.10	0.25	0.10
	35	0.25	0.30	0.15	0.10	0.25	0.10
	36	0.25	0.30	0.15	0.10	0.25	0.12
Aerator pH	25	6.7	6.6	7.8	7.7	7.8	7.9
	28	5.2	5.1	7.2	7.8	7.7	7.7
	30	5.4	5.4	7.7	7.7	7.8	7.9
	36	6.7	6.4	7.6	7.7	7.7	7.7
Aerator Dissolved							
O_2(mg/l)	25	6.9	6.6	7.8	7.7	7.7	8.1
	28	7.7	7.7	7.8	8.0	7.9	8.1
	30	7.9	7.9	8.9	8.8	8.7	8.9
	32	8.1	8.0	7.8	7.8	8.4	8.3
	35	6.8	7.0	7.4	7.7	7.1	7.8
	36	6.9	7.1	7.5	7.9	7.1	7.7

[*] Pesticide wastewater addition to test units was begun on day 14.

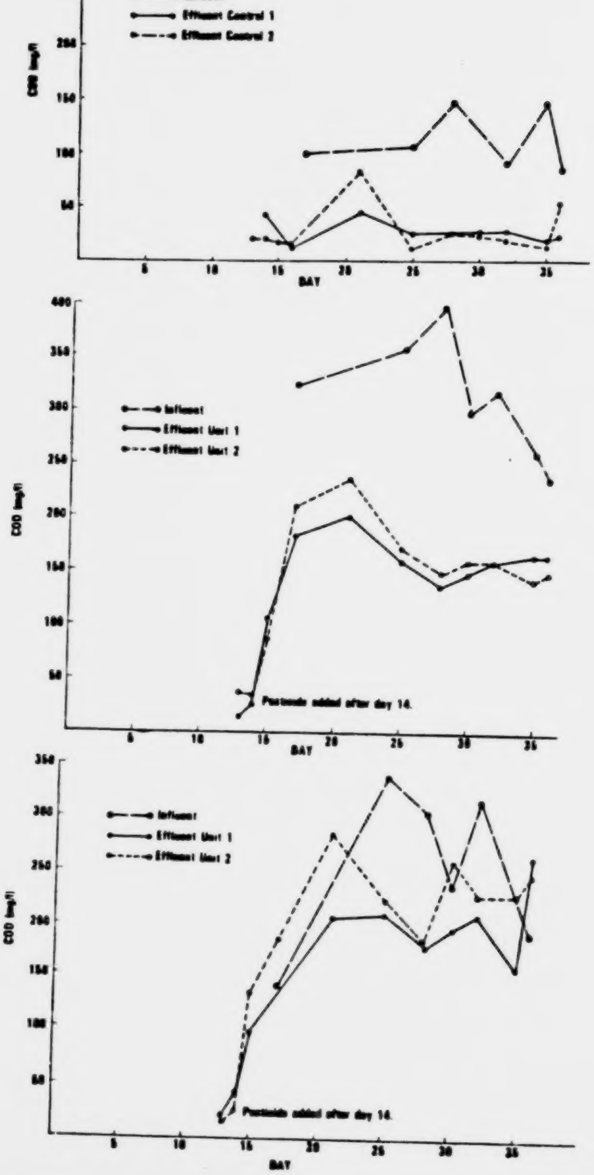


Figure 26. Influent and effluent COD for activated sludge units; (a) control units; (b) units fed Plant A wastewater; (c) units fed Plant B wastewater.

and effluents. At the late logarithmic and stationary phases, growth at the 1% wastewater concentration was greatly reduced, generally representing about ≤10% of that in the controls. At the 0.1% concentration, growth occurred in both influent and effluent, but was only about half that of the control.

Both influent and effluent from units fed Plant B wastewater totally inhibited growth at a 1:10 dilution (10%). In the stationary phase, growth was similar in both 1.0 and 0.1% influent concentrations, findings which must be considered suspect as one would expect to see more inhibition at the 1% level. As was the case with Plant A, Plant B effluents greatly reduced growth at a 1% concentration. At 0.1%, growth was nearly equal to that of the control. The influent was somewhat more inhibitory. Results of the algal assay tests may be summarized in terms of I_{14} as follows:

	I_{14}			
	10%	1.0%	0.1%	0.01%
Untreated full strength Plant A wastewater	96	97	98	9
Influent, Plant A wastewater (10% in domestic sewage)	100	95	65	-
Effluent, Plant A wastewater (10% in domestic sewage)	100	93	36	-
Untreated, full strength Plant B wastewater	99	68(?)	98	4
Influent, Plant B wastewater (10% in domestic sewage)	100	52	46	-
Effluent, Plant B wastewater (10% in domestic sewage)	100	95	21	-

In both cases, the toxicity of the wastewater was reduced somewhat, but not markedly, by AS treatment. The reduction certainly does not indicate that AS treatment of maneb manufacturing wastewaters, even at 1:10 dilutions, will be satisfactory for relieving toxicity to algae.

Toxicity to fish of the influents and effluents of control and test units was also determined (Appendix N, Table N-14). Influents and effluents of control units fed domestic sewage were not toxic to fish at 10% and 18% concentrations. The LC_{50} values would thus be >18%. Due to volume constraints, high concentrations could not be tested. In sewage supplemented with Plant A wastewater (10%, v/v), the fish assays gave anomalous results (40% survival at 100 ml/l and 70% survival at 180 ml/l), but in both cases this influent was more toxic than the domestic sewage alone. The effluent results were also anomalous and do not indicate whether or not toxicity was relieved. Volume constraints prevented repeating the tests. Sewage supplemented with Plant B wastewater was extremely toxic, as would be expected from the LC_{50} of the untreated wastewater (~0.18 ml/l, compared to ~1 ml/l for the Plant A wastewater). Activated sludge treatment greatly reduced the toxicity of this wastewater. Whereas at a concentration of 10% the influent killed all of the fish, 30-60% of the fish survived in effluent concentrations of 18%.

In summary, activated sludge treatment of maneb manufacturing wastewaters produced some reduction in COD and the system can operate at least marginally on sewage containing 10% of this wastewater. However, effluents from units treating these wastewaters contain very high levels of ETU (Table 36). The significance of ETU in these effluents must be investigated before AS can be recommended for treatment.

GAC treatment appears to offer several advantages as a choice for removing maneb, ETU and COD from maneb manufacturing wastewaters. However, GAC treatment systems should be monitored for ETU breakthrough, rather than maneb breakthrough, since ETU (1) breaks through first and (2) is potentially more serious from the standpoint of health impact.

The cost of the carbon treatment option dictates a search for alternative treatment methods. To this end, additional work will be undertaken to investigate the possible biological treatment of maneb wastewaters at concentrations other than those investigated in this study. Particular attention will be given to the fate of ETU in biological treatment systems and the impact of this wastewater on nitrification.

SECTION 8

LITERATURE REVIEW AND DISCUSSION

GENERAL CHARACTERISTICS OF PESTICIDE MANUFACTURING WASTEWATERS

Pesticide manufacturing wastewaters are as diverse as the pesticides themselves. The wastewaters vary greatly according to the nature of the product--its chemical composition, its physical state (i.e., oil, aqueous solution, crystal, powder, etc.), and its purity. However, it is possible to divide the myriad pesticides into five major classes and to make some generalizations about production, wastes generation, and treatability.

Hackman (1978) has concisely summarized the EPA development documents dealing with effluent limitations guidelines and come up with such a categorization. He notes that:

(1) "specific pesticide manufacturing operations are unique and generally characteristic only of a given facility"

(2) "few, if any, pesticide plants manufacture one product or use only one process", but "instead, almost all plants are multiproduct/-process facilities" with a unique mix of products

(3) many plants produce materials which are used on-site as feed stock for other products

(4) many plants produce materials other than pesticides.

He notes further that while there are over 500 commercially important pesticides and over 34,000 formulated products, the major divisions of pesticide products can be categorized as follows:

(1) halogenated organic (example: DDT) - broad activity spectrum, prolonged stability and residual activity.

(2) organophosphorus - highly toxic, usually hydrolyzed in alkaline medium to yield materials of relatively less toxicity, usually biodegradable.

(3) organonitrogen - very broad range of biological activity

(4) metallo-organic

(5) botanical and microbiological

(6) miscellaneous

Noted differences among the first three categories are as follows:

(1) Chlorinated hydrocarbons are much more persistent in the environment than the organophosphorus and organonitrogen compounds.

(2) the organophosphates and organonitrogen compounds are amenable to chemical hydrolysis.

(3) certain chlorinated hydrocarbons are amenable to recovery, such as by steam stripping.

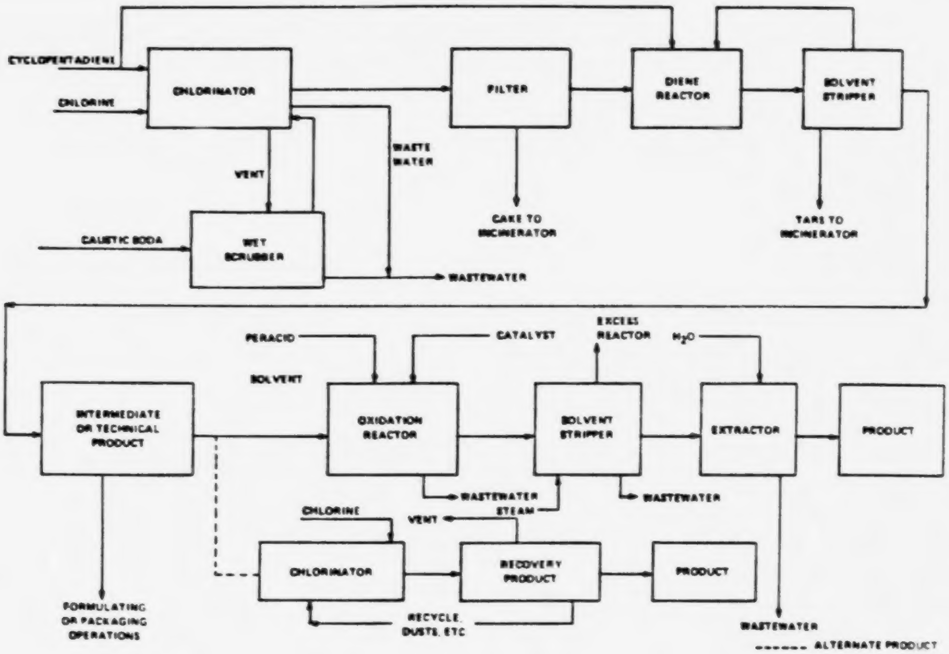
Information on production and waste generation is summarized in Tables 40-42.

General sources of information on characteristics of pesticides manufacturing wastewaters include Archer et al. (1978), Kelso et al. (1978), Nemerow (1971), Atkins (1972), Lawless et al. (1972), Ferguson (1975), Parsons (1977), Becker and Wilson (1978), and Hackman (1978).

It was not possible within the scope of this project to prepare an exhaustive review of all literature dealing with biological and physical chemical treatability of pesticides and pesticide-contaminated environmental media; impacts of pesticides on biota; and fate of pesticides in the environment. However, during the course of the project a great deal of information in these areas was accumulated. In the following sections this information is briefly reviewed and sources of further information, especially recent reviews and other compilations, are referenced.

Table 40. GENERALIZED SCHEME OF PRODUCTION AND WASTES GENERATION--HALOGENATED ORGANIC PESTICIDES (from Hackman, 1978).

General Process Flow Diagram for Aldrin-Toxaphene Production Facilities


CYCLOPENTADIENE
CHLORINE
CHLORINATOR
FILTER
DIENE REACTOR
SOLVENT STRIPPER
VENT
WASTE WATER
CAKE TO INCINERATOR
TARS TO INCINERATOR
CAUSTIC SODA
WET SCRUBBER
WASTEWATER
PERACID
CATALYST
EXCESS REACTOR
H2O
SOLVENT
INTERMEDIATE OR TECHNICAL PRODUCT
OXIDATION REACTOR
SOLVENT STRIPPER
EXTRACTOR
PRODUCT
WASTEWATER
STEAM
WASTEWATER
CHLORINE
VENT
CHLORINATOR
RECOVERY PRODUCT
PRODUCT
FORMULATING OR PACKAGING OPERATIONS
RECYCLE, DUSTS, ETC
WASTEWATER
------ ALTERNATE PRODUCT

Wastewaters generated in the production of this family of pesticides are:

1. Vent gas scrubber water from caustic soda scrubber
2. Aqueous phase from the epoxidation step
3. Wastewater from the water wash and product purification units
4. Periodic equipment cleaning wastewater
5. Wastes from cleanup of production areas

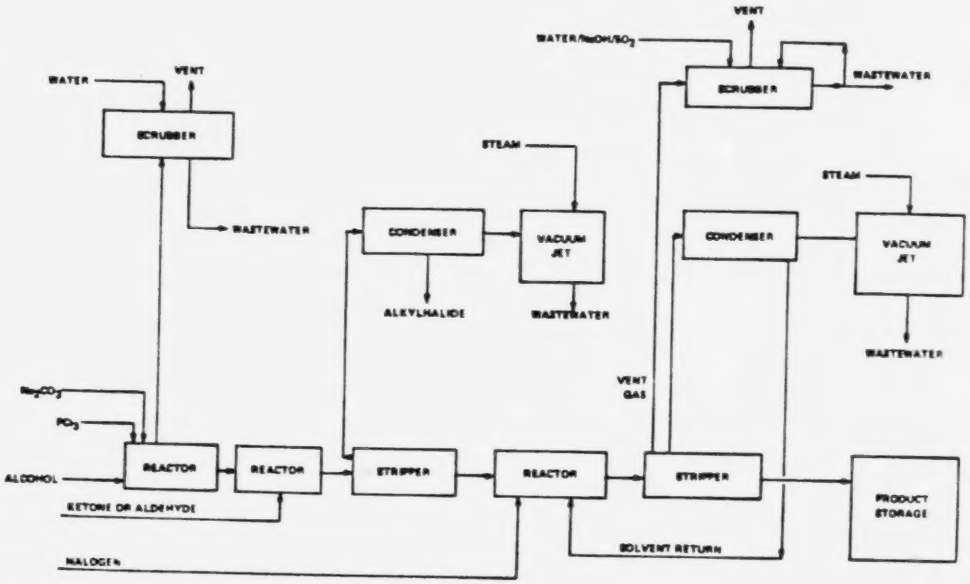
Tars, off-specification products and filter cake should not generate wastewaters since they are usually incinerated.

Halogenated Organic Pesticides Plant
Waste Loads

Production (small plant), kkg/day	16.2
Production (large plant), kkg/day	85.7
Flow, l/kkg	35.300
BOD, kg/kkg	97.2
COD, kg/kkg	183
TSS, kg/kkg	3.49
Phenol, kg/kkg	1.92
Total pesticide, kg/kkg	0.327

Table 41. GENERALIZED SCHEME OF PRODUCTION OF WASTES GENERATION--PHOSPHORUS-CONTAINING PESTICIDES (from Hackman, 1978).

General Process Flow Diagram for Phosphate and Phosphonate Pesticide Production Facilities

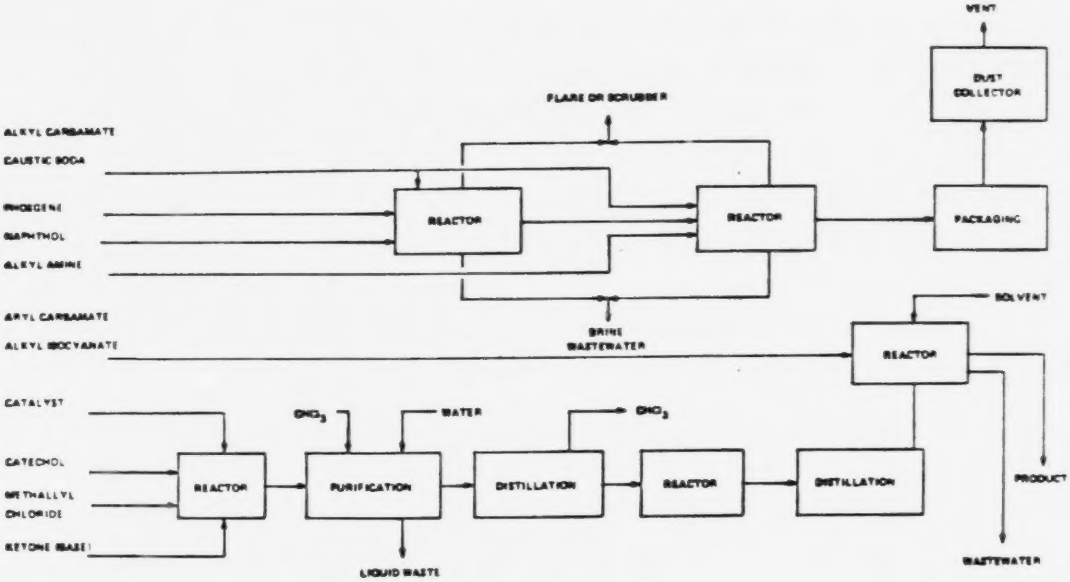

VENT
WATER/NaOH/SO2
WATER
VENT
SCRUBBER
WASTEWATER
SCRUBBER
STEAM
STEAM
WASTEWATER
CONDENSER
VACUUM JET
CONDENSER
VACUUM JET
ALKYLHALIDE
WASTEWATER
WASTEWATER
VENT GAS
Na2CO3
PCl3
ALCOHOL
REACTOR
REACTOR
STRIPPER
REACTOR
STRIPPER
PRODUCT STORAGE
KETONE OR ALDEHYDE
SOLVENT RETURN
HALOGEN

Organophosphorus Pesticide Plant
Waste Loads

Production (small plant), kkg/day	6.57
Production (large plant), kkg/day	72.0
Flow, l/kkg	43.900
BOD, kg/kkg	67.7
COD, kg/kkg	267
TSS, kg/kkg	11.7
NH_4-N, kg/kkg	81.8
Total pesticide, kg/kkg	0.454

Table 42. GENERALIZIED SCHEME OF PRODUCTION OF WASTES GENERATION--
ORGANONITROGEN PESTICIDES (from Hackman, 1978).

General Process Flow Diagram for Alkyl and Arylcarbamate
Production Facilities


VENT
DUST COLLECTOR
FLARE OR SCRUBBER
ALKYL CARBAMATE
CAUSTIC SODA
PHOSGENE
NAPHTHOL
ALKYL AMINE
REACTOR
REACTOR
PACKAGING
ARYL CARBAMATE
ALKYL ISOCYANATE
BRINE WASTEWATER
SOLVENT
REACTOR
CATALYST
$CHCl_3$
WATER
$CHCl_3$
CATECHOL
METHALLYL CHLORIDE
KETONE BASE
REACTOR
PURIFICATION
DISTILLATION
REACTOR
DISTILLATION
PRODUCT
LIQUID WASTE
WASTEWATER

Wastewaters associated with the production of these compounds are:

1. Brine process wastewater from reactors
2. Wastewater from the caustic soda scrubbers
3. Aqueous phase wasted following the isocyanate reaction
4. Reactor cleanout washwater
5. Area washdowns

Organonitrogen Pesticide Plant
Waste Loads

Production (small plant), kkg/day	9.43
Production (large plant), kkg/day	116
Flow, l/kkg	35.400
BOD, kg/kkg	45.5
COD, kg/kkg	103
TSS, kg/kkg	2.50
NH_4-N, kg/kkg	60.2
Total pesticides, kg/kkg	2.82

Activated Carbon Treatment of Pesticides, Pesticide-Contaminated Water and Pesticide-Manufacturing Wastewater

Carbon treatment is often the most cost-effective means of removing pesticides from water and wastewater. Use of activated carbon for this purpose was recently exhaustively reviewed by Becker and Wilson (1978) in a document also setting forth for major pesticides their production volumes; uses; classes; manufacturing and disposal techniques; waste production; toxicity and various treatment processes. In regard to activated carbon treatment, the following are reviewed: (1)industrial wastewater treatment installations using GAC treatment, (2) efficiency of carbon for adsorbing a variety of pesticides; (3) carbon dosages required for treating 2,4-D compounds, rotenone, toxaphene, "cube root", DDT, aldrin, and dieldrin; (4) adsorption isotherm data on several pesticides; (5) typical GAC facility flow diagram; and (6) six case studies including cost data.

Another review of AC treatment of pesticide wastewaters was that by Atkins (1972), who reviewed and summarized much of the work on adsorption of pesticides to AC and other sorbents and reprinted tables from much of the literature extant in 1972 (Robeck et al., 1965; Faust and Suffet, 1966; Sigworth, 1965; Aly and Faust, 1965; Cohen et al., 1960; Whitehouse, 1967). Where applicable, work of these authors is summarized below.

Sharp and Lambden (1955) and Lambden and Sharp (1960) described the wastewater treatment system at Fisons Pest Control Ltd., a British manufacturer of pesticides. The wastewater contains DNOC (dinitroorthocresol), DNBP (dinitro secondary butyl phenol), MCPA (2-methyl 4-chlor phenoxy-acetic acid), DDT, copper salts, sulphonated phenol and cresol, chlorinated cresol, intermediate nitro compounds, cresol, phenol, solvents, surface active agents, glycollic acid, amine salts, sodium sulfate, and sodium chloride, and the BOD_5 is about 2000-3000 mg/l. Pilot studies were described in the earlier article (Sharp and Lambden, 1955); the full scale plant, in the later article. The treatment plant incorporates three major processes:

(1) activated carbon pretreatment at neutral pH to remove toxic organics

(2) lime precipitation of toxic metals
(3) biological treatment.

Carbon regeneration is carried out on-site. The activated carbon system can reduce phenols from 160 to 5 mg/l and DNOC from 60 mg/l to trace levels. The authors stressed that the activated carbon pretreatment made possible further treatment by trickling filters and that this system had worked successfully at full-scale over a 5 1/2 year period. They stated however, that "Treatment costs are high, providing an incentive to reduce the load on the effluent plant by careful attention to the manufacturing processes."

Mitkalev et al. (1965) performed activated carbon studies on herbicide manufacturing wastewater. The wastewater contained 2,4-D derivatives. Activated carbon was stated to be an effective adsorbent, easily regenerated with 5% alkali at 70-80°C or by superheated water vapor at 250-300°C.

Ismail and Wardowski (1974 a and b) investigated effectiveness of activated carbon for removing the fungicide sodium o-phenylphenate (SOPP) from actual and simulated citrus packinghouse effluents. Powdered activated carbon (10 g/l) removed more than 99% of the phenolics from solutions and wastewaters. In aqueous solutions containing 100 mg/l of SOPP, 0.25% PAC removed 99.6% of the pesticide. In actual effluents containing 311 mg/l (as equiv. SOPP) 1% PAC removed 99.98% (1974 b). GAC column studies (1974 a) with large volumes of simulated effluents showed, as expected, decreasing removal efficiency with increasing volume treated. The initial efficiency was 81.5%.

Nemerow (1971) in his industrial wastes text notes the difficulties in treating pesticide wastewaters in municipal biological plants because of the toxicity of the constituents of the pesticide wastewater and the high costs of treating with activated carbon (for 2,4-D wastewaters about $6/lb of dichlorophenol removed, in 1959).

Minturn (1974) reviewed advanced wastewater technologies investigated by the Oak Ridge National Laboratory, including experiments on herbicide washwaters (water used in cleaning equipment used in manufacturing, storing, formulating, and spreading). Treflan and diphenamide were taken up "reasonably well" by PAC - Aqua Nuchar A, but paraquat was not as easily sorbed. It was noted that the paraquat tests were run in 0.02 M NaCl solution and that uptakes on PAC would have been higher at higher salt levels. It was also noted that high levels of carbon were required to treat herbicide washwaters with the levels of pesticides present (up to 1650 mg/l of paraquat; 318 mg/l treflan, and 156 mg/l diphenamid), thus making the cost unattractive unless some use could be found for the pesticide-saturated carbon. The potential for AC treatment of large volumes with low concentrations, as might be found in wastewaters from pesticide manufacturing, was considered more atttractive.

Bernardin and Froelich (1975) conducted both laboratory and plant scale tests to evaluate ability of GAC to adsorb organic toxicants. Their extensive study addressed (1) laboratory tests of applicability of carbon in removal of toxicants and (2) fish bioassay tests on influent and effluent from five industrial plants employing AC treatment. The five plants manufactured, respectively, (1) specialty chemicals, producing a low pH - high chloride wastewater, (2) specialty chemicals with a wastewater containing high TDS and some floating oil, (3) soap and detergent with high pH wastewater containing surfactants and organic amines, (4) phenolic resins, and (5) plastics. Laboratory adsorption isotherm tests with Filtrasorb 300 (Calgon Corp.) indicated that final concentrations of less than 1 microgram per liter could be obtained with a number of compounds. Fish bioassay tests with bluegill fish, using actual wastewaters, indicated total removal or significant reductions of toxicity after passage of the wastewater through the AC system.

Wilder (1976), in a letter report of EPA Effluent Guidelines Division, assembled field data on treatment of hazardous spills with AC columns, with or without such pretreatment as pH adjustment, flocculation, and filtration. One to three columns were employed at flow rates of 100-600 gpm and contact times of 8-60 minutes. Pollutant removal was high (96.11-99.98%) and consistent. The types of pesticide spilled and concentrations (as ppb) of the influent to the carbon columns are as follows:

toxaphene	36
dinitrobutylphenol	200
kepone	4000
PCBs	3.5
aldrin	60.5, 8.5
heptachlor	80, 6.1
dieldrin	64, 11
chlordane	1430, 13

Bunn (1975) in a letter report to EPA described treatment of several Chemagro wastewaters with Nuchar C-190 AC, 20 g/250 ml. The wastewater contained the pesticides sencor (a triazine type herbicide) and treflan (trifluralin). Sencor removals of 99.8% (from 13-15 mg/l to ∿0.03 mg/l) were achieved. Effect on trifluralin was not discussed. The wastewater appeared to exert toxicity in BOD tests.

Schwartz (1967) investigated removal of 2,4-D and CIPC [isopropyl N-(3-chlorophenyl)carbamate] from dilute aqueous solutions with PAC (Nuchar C-140) and with the clay minerals illite, kaolinite, and montmorillonite. The minerals were not effective even at concentrations of 800 mg/l, but adsorption of CIPC with PAC was extensive. Initial CIPC concentrations of 5.0 mg/l were reduced by 98% within 22 hr with 100 mg/l of carbon, with approximately 90% of the adsorption occuring within the first 4 hr.

Information from EPA indicates that the following pesticide manufacturing wastewaters are currently being treated with activated carbon:

ethalfluralin
benfluralin
dioxathion
carbofuran
terrazole
PCNB
propachlor
dodine
basagran
N-propamide
metham
carbendazin
DEET
piperonyl butoxide
chlorothalonil

Ability of GAC to reliably remove organics from potable water supplies was reviewed by Hager and Flentje (1965). Primary interest was in costs of removing odors from potable water.

Aly and Faust (1965) and Faust and Aly (1964) tested the effectiveness of activated carbon and other technologies on removal of 2,4-D and derivatives from natural waters. 2,4-D solutions were prepared using the sodium salt and water; commercial formulations of 2,4-D isopropyl ester and 2,4-D butyl ester were employed. Adsorption isotherm tests were conducted with Aqua Nuchar A (West Virginia Pulp and Paper Company) having a specific surface area of 550-650 m^2/g and a size of $\geq$ 325 mesh. Compared to oxidation ($KMnO_4$ and Cl_2) and ion-exchange [Dowex 1 (Dow-Corning Corporation); Amberlite IR-120 and IR-50 (Rohm and Haas Company)], activated carbon was the most effective method for removal of 2,4-D, 2,4-DCP, and the other derivatives. Amounts of carbon required to reduce 3.0 mg/l to 0.1 mg/l were as follows:

2,4-D, sodium salt	92 mg/l carbon
isopropyl ester	49 mg/l carbon
butyl ester	49 mg/l carbon
isooctyl ester	53 mg/l carbon

Evidently esters are sorbed more easily than the sodium salt. With 2,4-DCP an $\frac{x}{m}$ value of 0.0166 was achieved.

Cohen et al. (1960) conducted laboratory tests to determine if AC (Aqua Nuchar A, Westvaco) would remove low concentrations of rotenone and toxaphene from raw water (spring water). Adsorption isotherm studies were conducted and the treated solutions were subjected to fish bioassays. Amounts of carbon required for toxaphene and rotenone were similar. AC removed not only the poisons but also solvents and emulsifiers found in the commercial preparations. It was far more effective than chlorination and alum coagulation for removing these fish poisons. Curves were derived to enable rapid determination of amounts of carbon required to reduce a given poison concentration to a selected residual concentration.

Robeck *et al*. (1965) investigated effectiveness of water treatment processes in pesticide removal. The study was conducted in two 20-gpm pilot water treatment plants which included in the treatment train the following processes:

1) rapid mix with alum, activated silica, and activated carbon
2) flocculation
3) settling
4) filtration through sand or charcoal
5) optional 2-stage (series) activated carbon beds

In all pilot studies known quantities (∿ 1-25 ppb) of pesticide were added as an emulsion prior to the first process. Pesticides tested were DDT, dieldrin, endrin, lindane, 2,4-5-T ester, and parathion.

Adsorption isotherm curves were obtained in jar tests with distilled water and with river water. For these experiments a PAC (Aqua Nuchar A, Westvaco) slurry was employed. Because of the background organic material found in the river water, more carbon was required to reach the arbitrary concentration of 0.1 ppb. Competition among pesticides for sorption was also investigated. In river water with 10 µg/l (each) concentrations of lindane, dieldin, and parathion added, it appeared that dieldrin and lindane reacted the same as in single pesticide applications. However, for some unknown reason parathion removal appeared to be influenced by the presence of other pesticides and to a degree not accounted for by the minute amount of organic matter contributed by the other pesticides. Parathion was readily removed by PAC; a 5 mg/l carbon dose was capable of achieving > 99% removal of parathion at an initial load of 10 ppb. GAC studies demonstrated that as far as pesticides were concerned, they did not penetrate ahead of other organics. Overall conclusions reached were as follows:

1) DDT was readily removed in conventional water treatment processes (settling, coagulation, filtration); lindane and parathion were not.
2) Lindane, parathion, 2,4-5-T, and dieldrin were removed in conventional treatment followed by GAC filtration; 2-stage filtration was generally required to achieve residual levels of $\leq$ 0.1 ppb.

Sigworth (1965) of West Virginia Pulp and Paper Company conducted laboratory studies on removal of odor-causing pesticides from water. Effectiveness of treatment was evaluated by determination of threshold odor values and by chemical analysis. Powdered activated carbon was used, but type was not disclosed. The author states the "removal of 90 percent or more of the associated odors was readily accomplished with laboratory dosages in the range of 2-20 ppm of carbon." Specific results are as follows:

	Carbon dose	Pesticide Concentration, mg/l	
Pesticide	mg/l	Initial	Final
Parathion	10	10	2.6
BHC-37, gamma	5	25	0.08
Malathion (50%)	10	2	0.25
2,4-D (23.5%)	20	6	1.38
2,4-D (11.7%)	10	1	too low to detect
Chlordane (6%)	10	50	too low to detect
DDT (50%)	2	5	too low to detect

In connection with problems of insecticide contamination of livestock drinking waters, Goodrich and Monke (1970) conducted laboratory studies to:

1) determine ability of GAC to remove low levels of dieldrin from water,

2) determine size of the required GAC filter, and

3) evaluate radioactive tracer techniques for low level insecticide detection.

Commercial grade activated carbon (Grade ACC derived from petroleum residue) was employed in four size ranges, U. S. standard sieve (1) 6-8, (2) 8-10, (3) 10-12, and (4) 12-14. GAC removed up to 99% of dieldrin from a solution containing 65 ng/l. Size of carbon granules in the range tested had no significance. The authors concluded that a GAC filter could protect against the insecticide in a rural water source.

Eichelberger and Lichtenberg (1971) tested the efficiency of the standard carbon adsorption method (CAM) for recovery of 11 organochlorine and 10 organophosphorus pesticides from water. A mixture of 21 pesticides, each at 2 μg/l concentration, in Cincinnati tapwater was applied at 130 ml/min to carbon cartridges containing Nuchar C-190. Pesticides were lindane, heptachlor, aldrin, heptachlor epoxide, DDE (p,p'), DDT, endosulphan, dieldrin, endrin, methoxychlor, chlordane, def, malathion, parathion, azodrin, trithion, bidrin, fenthion, methyl parathion, ethion, and methyl trithion. After passage through the carbon, the water showed no pesticide content above minimum detectable concentrations of 10 ng/l of organochlorine and 25 ng/l of organophosphorus compounds. Therefore, adsorption was very efficient.

The pesticide antimycin can be removed by AC according to Dawson and Marking (1974). A solution containing 100 times the lethal concentration was detoxified by passage through a 15 cm filter of AC (20 x 40 mesh carbon). The sorptive capacity of the carbon was found to exceed 3 mg/g.

Gomella and Belle (1975) determined adsorption isotherms with a variety of carbons and a number of test compounds including aldrin, dieldrin, 3,4-benzopyrene, lindane, and endosulfan. At a 20 mg/l carbon dose, two PACs were capable of removing $\geq$ 99% of aldrin from a solution with initial concentration of 100 μg/l. One carbon was able to accomplish similar removals with lindane, dieldrin, and 3,4-benzopyrene. As noted in other studies, application in several doses, rather than all at once, allowed considerable reduction in amount of carbon required.

Sigworth and Smith (1972) reviewed potential of activated carbon to remove trace metals from drinking water. Arsenic is listed as having a high adsorption potential in the higher oxidation states, whereas Zn and Mn are listed as having only slight potential.

Examining the possible use of adsorbents to protect crop roots, Coffey (1967) investigated activated carbon adsorption of herbicides, including the effect of carbon type, pH, and other factors. Eight pesticides were tested: CIPA, trifluralin, 2,4-D, diphenamid, DCPA, DNBP, amiben, and paraquat. Carbon types included Darco KB, Darco M, Hydro Darco B, and Darco G-60. Darco G-60 had the greatest sorptive capacity. Trifluralin and CIPC were most readily absorbed by carbon, while paraquat, a cationic herbicide, was not sorbed well. Under the conditions used, pH had little effect on carbon sorption.

Ward and Getzen (1970) investigated influence of pH on adsorption onto activated carbon of three carboxylic acid herbicides - 2,4-D, dicamba, and amiben. Absorption data were obtained in laboratory studies using Pittsburgh Chemical Company Type BL activated carbon. The herbicides were obtained as crystals and prepared as aqueous solutions. In all cases, lowering the pH below 7.0 markedly increased removals with maximum adsorption being obtained near the point where pH = pKa. This behavior, the authors believe, might help explain the tendency of these pesticides to accumulate in acidic, high organic soils.

ICI (1974) has tabulated published data on activated charcoal in agriculture, giving some indication of other pesticides which might be treated with AC. According to its summary the following pesticides should be sorbed onto AC:

Alachlor
Aldrin
Amiben
Amitrol-T
Atrazine
Azak 10
Bandane 35
Bensulide
Bromacil
CIPC
Chlordane
Chloroxuron
DCPA
DDT
DMPA, bensulide
DMTT (mylone)
DDVP
Ingram[sic] (igran?)
Isocil
Karsil
Lindane
Linuron
Mecoprop 3
Methoprotryne
Metribuzin
Monuron
Neburon
Nitralin
Norea
Oryzalin
Paraquat
Parathion
Pebulate
Pichloram

Dichlorbenil
Dieldrin
Dimoben[sic] (dinoben?)
Diquat
Diuron
EPTC
Endrin
Eptam
Ethyl-n-ethyl-n-cyclohexylthiol-carbamate
Fenac
Fluometuron
Heptachlor
IPC
Planavin 1.5
Prometryne
Propazine
Sesone
Siduron
Silvex
Simazine
TCA
Terbacil
Tricamba
Trifluralin
Vernolate
2,4-D
2,4-5-T

In summary, activated carbon treatment is capable of reducing concentration of many pesticides to below detectable levels. Much of the extant work, however, has been performed on laboratory-prepared solutions, surface waters, and potable waters. Pesticide manufacturing wastewaters, on the other hand, are quite complex and as shown in this project, may contain other non-pesticidal components which may contribute a major portion of the toxicity to aquatic organisms. Industry has stressed the need for realistic performance criteria for AC treatment of organic chemical manufacturing wastewaters (Lawson and Hovious, 1977), pointing out that laboratory studies should be followed by on-site continuous adsorption studies because of such factors as:

1. Plant-to-plant variations in adsorption performance.
2. Variability of production output and carbon performance with time in a specific plant.
3. Dynamic adsorption/desorption interactions in continuous carbon systems which are not predictable from isotherm tests.
4. Low predictability from batch isotherm tests of degree of removal and economic feasibility of removal of organics by continuous adsorption processes.

Shumaker (1977) also pointed out that, in an actual case study with an organic chemicals production plant, the AC unit treatment costs were higher than predicted and that care had to be exercised in selecting wastestreams to be put through the system. He noted that the AC system was ineffective in treating benzene sulfonates or low-molecular weight organics such as methanol, formaldehyde, and urea. He concluded that "while it has been demonstrated that activated carbon can be effectively utilized in treatment of complex chemical waste streams, it has also been demonstrated that carbon treatment is not a panacea for all chemical waste problems." As noted in this project, we found that removal of pesticide with GAC is not equivalent to removal of COD or toxicity.

OTHER PHYSICAL AND CHEMICAL TREATMENT METHODS

Several other methods of pesticides removal from water and wastewater are described in the literature.

Standard water treatment processes (chlorination, ozonation, uv-ozonation, flocculation) may effectively remove many pesticides (Robeck et al., 1965; Bauer, 1972); however, it is necessary to take care to insure that chlorination or ozonation does not produce other toxic products (Robeck et al., 1965).

Many organophosphorus and organonitrogen pesticides are susceptible to destruction by acid or alkaline hydrolysis (Hackman, 1978; Shih and Dal Porto, 1975; Ferguson, 1975). In many cases, rate of destruction is increased by increasing temperature. As pointed out by Hackman (1978), hydrolysis can be especially effective when used on segregated water streams since acid or base additions, thermal requirements, and size of equipment are minimized with these more concentrated flows. Hydrolysis is frequently useful in dealing with small amounts of "leftover" pesticides or with waters from washing pesticide application equipment. Care must be taken that toxic products are not formed during heating or hydrolysis. If complex pesticide manufacturing wastewaters are to be treated, even greater care must be taken since other components (such as solvents) may also produce toxic or otherwise dangerous products.

Sorbents other than AC may be useful in treating pesticide wastewaters. Kennedy (1973) described a process for treating chlorinated pesticide waste effluents, employing XAD-4, a synthetic polymeric adsorbent with high porosity, high surface area, and an inert, hydrophobic surface, capable of regeneration with an organic solvent (isopropanol) in such manner that the adsorbed pesticides can be recovered in concentrate form. With an actual wastewater from manufacture of a chlorinated pesticide, the leakage of unadsorbed pesticides from XAD-4 columns was "significantly lower" than from an activated carbon column. An economic analysis indicated that a combination of XAD-4 treatment with chemical regeneration would be more cost-effective than GAC and external thermal regeneration ($0.83/1000 gal vs. $1.33/1000 gal, assuming an influent with 200 ppm total chlorinated pesticides; pH 1.0; 150,000 gpd, run to 1 ppm leakage). Kunin (1976) reported more extensive studies on application of XAD resin treatment to a variety of wastewaters, including those from manufacture of chlorinated pesticides. According to Kunin, the XAD-4 resin was "clearly superior to the conventional carbon adsorbents."

Physical removal of certain pesticides from water can be accomplished by reverse osmosis (Edwards and Schubert, 1974; Chian et al., 1975). According to Edwards and Schubert, pesticides of low aqueous solubility (i.e., DDT) are more easily removed than more soluble types (such as 2,4-D). These authors noted that performance with mixtures of several solutes (as would be found in pesticide manufacturing wastewaters) may be considerably different from projections based on studies with individual components. Chian et al. (1975) found that cellulose acetate and cross-linked polyethylenimine membranes gave "excellent performance" in removing a variety of pesticides, including chlorinated hydrocarbon and organophosphorus types. More polar pesticides, such as atrazine, were not as readily removed, and it appeared that mechanism of removal was due to both polarity of the solute and adsorption of the pesticide onto the membrane materials. It was stated that "higher concentration of pesticides in the feed" would have adverse effects on performance, leading one to question applicability of reverse osmosis procedures to pesticide manufacturing wastewaters.

Sufficiently concentrated pesticide wastewaters may be treated by incineration (Carnes and Oberacker, 1976; Hackman, 1978; Ferguson, 1975). Temperature requirements vary with the specific pesticide. Potential problems include high fuel costs and generation of toxic gases (for example, CN from incineration of organonitrogen pesticides).

BIOLOGICAL TREATABILITY

Biodegradability of Pesticides

Degradation of pesticides in soils and other environments has been extensively and recently reviewed by Sanborn et al. (1977), Howard et al. (1975), Blanck et al. (1978), Edwards (1973), Haque and Fried (1975), Gillett et al. (1974), Kearney et al. (1969), Kearney and Kaufman (1975), Khan (1977), Malakhov and Duttweiler (1978). The report by Sanborn et al. (1978) is particularly relevant to disposal of pesticide-containing wastes. It reviews the published literature dealing with behavior in soil of 45 pesticides (including 17 herbicides, 20 insecticides, 6 fungicides, a fumigant, and an acaricide). In each case, information, if available, is included on (1) biological, chemical and physical degradation; (2) transport in soil and water; (3) volatilization; (4) uptake by organisms; (5) persistence, and (6) effects on nontarget organisms. The authors concluded that of the 45 pesticides reviewed, 10 were suitable for soil disposal, 21 were unsuitable, and in 14 cases available data were insufficient for conclusions. Of particular relevance to our project, these authors note that "since most of the available data deal with relatively small amounts of well-dispersed pesticides and degradation is almost invariably inversely correlated with concentration, bulk disposal of most pesticides will lead to long periods of persistence of the parent compound and/or its degradation products." Further, as we found in the course of our work, in actual pesticide wastewaters there are not only pesticides but many other components whose effects may be more serious than those of the pesticide or whose presence may affect pesticide degradation. Sanborn et al. (1977) summarized their review in a table, which is reproduced as Table 43. Feasibility of soil disposal was based on whether or not the pesticides would degrade in the soil environment. The authors also pointed out that incinerating pesticides would be a rapid efficient mode of disposing of many pesticides. In connection with our project, however, it must be recognized that the large quantity of water in the effluent would vastly increase thermal requirements for treatment.

In Table 43, several compounds studied in our project are included. Atrazine was not recommended for soil disposal because there was no evidence for degradation of the triazine ring under environmental conditions. The finding of atrazine and metabolites in many surface waters also indicates its persistence. We noted that while atrazine was readily (though not cheaply) removed by GAC, it was not very susceptible to biological treatment. Therefore we would agree with Sanborn _et_ _al_., that it would not be wise to rely on biological activity for disposal of "an already pervasive contaminant of uncertain biodegradability."

As we found, maneb did not persist long in the environment, but was rapidly converted to other compounds and eventually to ETU. Therefore, we reached the same conclusions as Sanborn _et_ _al_.: "All methods of disposing of the dithiocarbamate fungicides...must take into account the carcinogenic metabolite ethylene thiourea."

Trifluralin is closely related to oryzalin which was investigated in this project. Sanborn _et_ _al_. (1977) noted that while it is not very toxic to mammals, it is highly toxic to aquatic organisms, highly persistent and magnified in aquatic food chains. Oryzalin is less toxic to fish and is also less persistent in the soil, persisting about 2-3 months compared to 5-6 months for trifluralin (Helling, 1976). Helling (1976) noted that dinitroaniline herbicides degrade more rapidly under anaerobic than aerobic conditions, produce numerous metabolites that tend to become associated with soil organic matter as bound residue, and appear (on the basis of limited evidence) to have no lasting effects on soil microorganisms. We found that oryzalin itself was not a problem in the production wastewaters, but that persistence of the colored metabolites and presence of other toxic materials, expecially ammonia, were factors controlling treatability.

Sanborn _et_ _al_. (1977) did not review literature dealing with organoarsenicals. However, other information on MSMA indicates that it is broken

Table 43. FEASIBILITY OF SOIL DISPOSAL FOR 45 PESTICIDES [from Sanborn et al., (1977)]

Herbicide	Soil disposal	Insecticide	Soil disposal	Miscellaneous	Soil disposal
Atrazine[a]	no	Aldrin	no	Captan	yes
Bromacil	?	Chlordane	no	Dicofol	no
CDAA	?	Chlordecone (Kepone)	no	Dodine	?
Chloramben	yes	DDT	no	Maneb[a]	?
2,4-D	yes	Dieldrin	no	Methyl bromide	no
Dicamba	?	Endosulfan	no	Nabam[b]	?
Diquat	no	Endrin	no	Pentachlorophenol	no
Diuron	no	Heptachlor	no	Zineb[b]	?
EPTC	yes	Methoxychlor	yes		
Linuron	no	Mirex	no		
Monolinuron	no	Toxaphene	no		
Monuron	no	Azinphosmethyl	?		
Nitralin	yes	Diazinon	?		
Paraquat	no	Disulfoton	?		
Picloram	no	Malthion	yes		
2,4,5-T	?	Methyl parathion	?		
Trifluralin[b]	yes	Parathion	?		
		Phorate	?		
		Carbaryl	yes		
		Metalkamate (Bux)	yes		

[a] Indicates compounds investigated in this project.

[b] Closely related to compounds investigated in this project.

down in soils, at least partially, by biological activity (von Endt et al., 1968). As pointed out in Section 6, however, elemental arsenic is produced. Fate of arsenic itself is the critical factor in final disposition of MSMA wastewaters.

The processes of nitrification and denitrification are important in the soil nitrogen cycle and may also be important in operation of advanced biological wastewater treatment facilities.

Bartha et al. (1967) determined the influence of 29 pesticides on aerobic activities (CO_2 production and nitrification) of soil microorganisms. Effects fell into 3 categories:

(1) Compound was stable and without significant effect (chlorinated hydrocarbons)

(2) Compound persisted and depressed respiration and nitrification (carbamates, cyclodienes, phenylureas, thiocarbamates)

(3) Compound displayed toxicity but was transformed by soil organisms (amides, anilides, organophosphates, phenylcarbamates, triazines).

Analytical grade chemicals and sandy-loam soil were studied in laboratory scale studies. CO_2 production was measured volumetrically over a 30 day period and nitrification was indicated by increased nitrate over time during incubation at 28°C for 18 days. Test levels were greatly in excess of normal pesticide usage. The pesticides tested included atrazine and carbaryl.

Atrazine was tested at 500 and 1000 ppm. At 500 ppm, it retarded nitrification, but ability to do so decreased with time, indicating the herbicide was transformed and detoxified or that a resistent nitrifying population was developed. The atrazine molecule was degraded in soil. Atrazine and simazine were very different in terms of effect on CO_2 production, possibly due to ability of several organisms to produce CO_2 from ethyl amino side chains but not from the s-triazine itself. Atrazine also more effectively inhibited nitrification and depressed soil respiration.

Carbaryl was tested at 150 and 1500 ppm. At 150 ppm, it retarded nitrification but ability to do so decreased with time. Carbaryl has a half-life of 7 days in soil. At both test concentrations, carbaryl depressed CO_2 production and the effect persisted for some time. Added glucose reduced the degree of inhibition of CO_2 production by about 50-60 percent.

Bollag and Henniger (1976) investigated influence of pesticides on denitrification and found that captan, maneb, nabam, and (to some degree) 2,4-D inhibited denitrification by soil microorganisms. Carbaryl, phenylurea herbicides, and propham were less inhibitory. We noted that sludge collected from AS units fed maneb wastewaters did not undergo the darkening and gasification exhibited by the sludge in the control units.

Treatment of Pesticide Manufacturing Wastewaters

While most pesticide manufacturers have been reluctant to divulge information about the effectiveness of their waste treatment procedures, the published literature does contain some case studies.

In 1961 Monsanto completed a full-scale wastewater treatment plant at Anniston, AL for the treatment of parathion wastewaters (Anon, 1961). The plant was reported to successfully treat wastewaters containing paranitrophenol, organophosphorus compounds, sulfides, and other components and to reduce BOD from 4000 mg/l to 13 mg/l. Treatment steps included:

1) Limestone neutralization to raise pH from ∿ 1 to 6.8,
2) Equalization, and
3) Acclimated activated sludge.

The sludge was fully acclimated to undiluted parathion wastewater. Aeration capacity of 30 ft^3/lb BOD/day was supplied. A removal of 90-98% of the phenolics was achieved.

Stutz (1966) reviewed the first 9 years of experimentation, pilot plant testing, and wastes (liquid, solid) treatment at this plant. Initially the wastewater was to be treated in conjunction with a municipal treatment plant, but the increased production necessitated construction by Monsanto of its own plant. The aerobic biological treatment system included 5-9 days detention time with a mixed liquor suspended solids level of 15,000-18,000 mg/l. Typical treatment achieved was reported as follows:

Parameter	Raw Wastewater	Plant Effluent
COD, mg/l	3,000	100
Total solids, mg/l	27,000	18,000
pH	2	> .0
Parathion, mg/l	?	<0.1
p-Nitrophenol, mg/l	?	<0.1

Further details of parathion treatment are given by Coley and Stutz (1966). Although Monsanto has been successful in treating parathion wastewaters with AS, other parathion manufacturers have not been able to duplicate its success.

Lue-hing and Brady (1968) described Chemagro's biological treatment of wastewaters from manufacture of organophosphorus pesticides, among them Co-Ral® (= coumaphos), Dasanit® (= fensulfothion), Baytex® (= fenthion), Di-Syston® (= methyl demeton), and Systox® (= demeton). Raw wastewaters contained residues from ∿ 30 different formulations of organophosphorus pesticides and were characterized by high BOD and COD, moderate SS, toxicity, a heavy layer of scum, and high organic phosphate concentrations.

Certain wastewaters difficult to treat alone have been treated successfully when mixed with municipal sewage. This proved to be the case in treatment of chlorophenolic herbicide wastewaters generated at Jacksonville, AK (Evans, 1971; anon., 1973). The plant produces 2,4-D and 2,4,5-T. Prior to the combined treatment, the plant wastewater had been treated only by neutralization prior to discharge into a receiving stream. After neutralization, the wastewater was still high in organic load and caused odors, off-tastes in fish and fish kills.

Successful treatment was achieved as follows:

1) pretreatment by industry
    a) skimming and sumps to remove light or heavy liquid phases
    b) neutralization to pH 5.3-5.8 by passage through cruised limestone
    c) equalization
    d) further pH adjustment to pH 7.2 with slaked lime slurry

2) Combined industrial municipal treatment
    a) biofiltration ("clarigester-filter")
    b) aerated lagoon with 3 days detention time and 745 $lb/O_2/hr$ aeration
    c) stabilization ponds

The following were noted:

1) domestic sewage bacterial flora readily degraded complex chlorophenols, glycolates, and acetates

2) high NaCl levels did not adversely affect biological activity

3) complaints of off-taste and odor in fish and in water ceased.

The entire treatment system removed 87-94% of the chlorophenols and 49-80% of the chlorophenoxy acids. The final effluent averaged 15 mg BOD_5/l; 0.1 mg/l of chlorophenols; and 1.1 mg/l of chlorophenoxy acids.

Wastewater from other industries may also contain pesticides. Wastewater from scouring rug wools mothproofed with dieldrin are difficult to treat. Wilroy (1964) described a successful treatment system developed for one large manufacturer. The wastewater from processing 50,000 lb wool/day would contain grease, 2400 lb; SS, 4200 lb; BOD_5, 2250 lb; and nonionic detergents, in a volume of 60,000 gal. The associated dye wastewaters would contribute 140,000 gpd containing grease, 310 lb; SS, 290 lb; BOD_5, 790 lb; dyes, 2000-3000 gal. In addition, 12000-15000 gpd of sanitary wastes would be contributed. A treatment system was designed with the following unit processes:

(1) fine screens on dyeing and scouring lines
(2) sedimentation, 6 hr detention, on wool scouring lines
(3) equilization and lagooning in 3.5' deep ponds, ~80 days detention time.

The treatment time was observed over the first year of operation. In the lagoon active anaerobic decomposition occurred, achieving an overall BOD reduction of 80-90% (effluent BOD_5 averaging 130 mg/l) and a dieldrin removal of about 99% (effluent concentration averaging 0.25 mg/l). The receiving stream contained red-breasted bream for which the TL_{50} for dieldrin is 8 ppb; however, sufficient dilution of the wastewater was provided to reduce the dieldrin to 0.5 ppb. In addition dieldrin was probably removed onto suspended solids and thence into the sediments, since this phenomen is known to occur with endrin, a related compound.

On the other hand, Garrison and Hill (1972) found that a total detention time of 7 days in a series of three 4-ft deep anaerobic lagoons removed only 10% or less of the dieldrin in wool scouring wastewaters from a carpet mill. Influent and effluent from the system both averaged 0.4 mg/l dieldrin. High dieldrin levels, up to 124 mg/l, were found in caddis fly larve collected in the river 4 miles below the outfall. The wastewater at this plant contained dyes, salts, and surfactants, but evidently did not contain domestic sewage, as did the plant described by Wilroy (1964). The dyes were also different. The plant described by Wilroy contained certain red and black dyes, while the plant described by Garrison and Hill contained anthraquinone blue disperse dyes and the carriers associated with their application. The blue dyes were not completely degraded during anaerobic treatment.

Some investigators have performed laboratory studies of pesticide degradation using organisms associated with biological treatment. Halvorson *et al*. (1971) developed a method for testing biodegradability of insecticides using resting cell preparations of bacteria from a sewage lagoon. Rates of degradation of organophosphorus insecticides (malathion, parathion, diazinon) were compared to those of chlorinated hydrocarbon insecticides (heptachlor, dieldrin, DDT). Analytical grade preparations of the insecticides were used. The experimental procedure was as follows:

1) concentrate and wash bacteria from sewage lagoon water
2) suspend in phosphate buffer (final concentration about 4×10^8 cells/ml)
3) add standard insecticide solution
4) incubate
    a) aerobic studies: incubate on a shaker
    b) anaerobic: flush container with nitrogen, close completely, keep stationary

5) at intervals remove aliquots of suspension for insecticide analysis.

The procedure for measuring biodegradation of chlorinated hydrocarbons was similar.

The organophosphate insecticides were quickly degraded by the bacteria. Presence or absence of oxygen appeared to have little effect with the exception that the suspension exposed to diazinon appeared to remain active longer in presence of oxygen. In order of increasing lability, the insecticides were ranked malathion > parathion > diazinon. On the other hand, chlorinated hydrocarbons were very resistant to biodegradation. Presence or absence of oxygen had no effect. Under anaerobic conditions DDT was quickly converted to DDD which was not further metabolized.

The authors felt that use of concentrated resting cell preparations had several advantages over use of growing cultures, such as (1) completion of test in hours rather than weeks or months, (2) ease of measuring degradation rate in the relatively "clean" preparation, (3) ready detection of acclimation or adaptation, and (4) feasibility of testing several insecticides at once since their studies showed that rate of use of any one pesticide was unaffected by presence of others.

Canter *et al*. (1969) used BOD and COD tests to evaluate effect of commercial pesticide products on oxygen demand of wastewater using BOD and COD tests. Toxicity of the preparations was assessed with BOD tests and with *Escherichia coli* (as measured by streaking plates containing the pesticide). Presence of commercial preparations of dieldrin and endrin markedly increased BOD of domestic sewage: dieldrin, BOD increased by 130 mg/l per mg/l of pesticide; endrin, by 40 mg/l per mg/l pesticide. Pure endrin alone exhibited no additive effect. Neither in concentrations up to 50 mg/l had any toxic effect in BOD tests. COD was also increased by addition of commercial preparations and the increase in COD was greater than for BOD, possibly due to the greater susceptibility of the organic solvents to biological than to chemical oxidation.

Toxicity to *E. coli* was low. *E. coli* grew for 24 hr in the presence of commercial preparations of up to 500 mg/l. At 3000 mg/l the *E. coli* could survive and grow in the presence of dieldrin but not endrin. In growth studies 600 mg/l of endrin was the highest concentration at which *E. coli* could survive for 14 days. The importance of pesticide solubility was stressed. Both dieldrin and endrin have low solubility in water and at concentration > 5 mg/l form colloidal sols which are physically unavailable to bacteria and thus show no toxic effect at up to 600 mg/l.

Vaicum and Eminovici (1974) described the effects of trinitrophenol and γ-hexachlorocyclohexane on the biochemical characteristics of activated sludge. Object of the laboratory and field studies was to see if certain biochemical measurements could be used to provide a means of early detection of toxic wastes.

For the laboratory studies continuous AS units were used. Three synthetic substrates with a COD of 400 mg/l were prepared for feed. They included (1) nutrient broth, glucose, aniline, dipotassium phosphate, ammonium sulfate; (2) as above, but without aniline; and (3) sodium acetate, urea, dipotassium phosphate. The units were allowed to operate at steady-state for three months. Then test compounds were added. Respiration rate, enzymatic activity (catalase and dehydrogenase), and protein content proved to be sensitive indices of the sludge activity. There appeared to be threshold concentrations of the test compounds which if exceeded led to irreversible damage to the sludge.

As might be expected, pesticides have also been found in biological wastewater systems not associated with the pesticide industry. Liu *et al.* (1975) sampled anaerobically digested chemical sewage sludges for chlorinated hydrocarbon pesticides. The studies were conducted at 4 plants in Ontario, where phosphorus removal is required. Iron sludge from a heavy industry area had the highest pesticide concentration (103 μg/l); iron sludge from a medium industry area, 63 μg/l; alum sludge from a light industry area, 45 μg/l; and lime sludge from a residential area, 20 μg/l. Lindane, dieldrin, aldrin, heptachlor and heptachlor epoxide, γ-chlordane, d-chlordane, O,P'-DDT, P,P'-DDT, P,P'-DDE, and P,P'-DDD were found in all sludges; heptachlor, chlordane, DDT, and DDT accounted for over 85% of the total. The presence of DDE and DDD indicated some transformation of DDT during treatment. Since DDT had been banned for some time, either the DDT persisted for a long time or some DDT was still being discharged illegally. There were no seasonal trends in type and quantity of pesticides. The presence of pesticides in sludge may possibly be a consideration if sludges are to be spread on land, although the total amounts applied at present should pose no problem according to the authors.

Jensen et al. (1972) identified another metabolite of DDT in anaerobic digested sewage sludge and lake sediment. In their work a liter of activated sludge was fed 100 mg P,P'-DDT fortified with ^{14}C-DDT and containing as contaminants DDD (4%) and DDE (3.1%). The sludge was incubated at 20°C for 8 days in a nitrogen environment, and aliquots were removed for pesticide analysis. DDT had a half life of 7 hours, and the original DDE disappeared in 48 hours. The DDT was transformed to DDD, DBP (P,P'-dichlorodiphenylbenzophenone), DDMU [(1-chloro-2,2-bis-(p-chlorophenyl)-ethylene)], and a newly identified product identified as DDCN [bis-(p-chlorophenyl)-acetonitrile]. This new compound was also found in a lake sediment--the first time it has been found in nature. After transformation to DDD and DDCN, no further transformation of DDT occurred. DDCN is patented for use against soil organisms.

In conclusion, there is a great deal of published information on biodegradation of some pesticides, especially in the soil environment. On the other hand, there are many pesticides for which information is sparse or nonexistent. Published case studies of biodegradability of actual pesticide manufacturing wastewaters, which are multicomponent and which tend to vary greatly in strength, are very limited in number and scope. Such studies, accompanied by (1) precise and complete chemical characterization; (2) assessment of effects on biological treatment organisms, including those responsible for aerobic degradation, anaerobic degradation, nitrification, and denitrification, and (3) assessment of impact on receiving stream organisms, are sorely needed to develop control technology which is both cost-effective and environmentally sound.

SECTION 9

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APPENDIX A

ANALYTICAL PROCEDURES FOR ROUTINE WASTEWATER CHARACTERIZATION

Routine wastewater analyses were conducted according to Standard Methods for the Examination of Water and Wastewater, 14th Edition, (APHA, AWWA, WPCF, 1976).

pH--

pH was determined electrometrically by Method 424.

Chloride--

Chloride was measured by the mercuric nitrate method (Method 408 B).

Acidity--

Acidity, as $CaCO_3$, was determined by Method 402.

Alkalinity--

Alkalinity, as $CaCO_3$, was determined by Method 403.

Nitrogen Forms--

Total Kjeldahl nitrogen was determined after digestion, according to Method 421. Ammonia (NH_3-N) was determined by an acidimetric method as described in Sections 418 A and 418 D. Nitrite and nitrate nitrogen (NO_2-N, NO_3-N) were determined by the Devarda's alloy method (419 F).

Phosphorus--

Total phosphorus (TP) was determined by the ascorbic acid method (425 C and F).

COD--

Chemical oxygen demand (COD) was determined by Method 508.

Residues--

Suspended solids (SS) were determined by Method 208 D. Total solids (TS) were determined by Method 208 A. Total dissolved solids (TDS) were determined by Method 208 A. Settleable solids were determined by Method 208 F.

APPENDIX B

ANALYTICAL PROCEDURE FOR ARSENIC

Analysis for arsenic was performed using a Perkin-Elmer Model 403 atomic absorption spectrophotometer equipped with an HGA-2000 graphite furnace and a deuterium arc background corrector. The samples were diluted 9:1 sample: 1.75% HNO_3 solution containing 10,000 ppm nickel. Calibration standards were prepared from stock 1000 ppm arsenic solution and diluted like the samples with 1.75% HNO_3 solution containing 10,000 ppm nickel. Previous work in our laboratory has shown that an organo-arsenic compound gives approximately 80% of the instrument response as an inorganic standard for the same weight of arsenic, with some variation due to a concentration effect. Calibration and instrumental data are shown in Table B-1.

Table B-1. CALIBRATION AND INSTRUMENTAL DATA FOR ATOMIC ABSORPTION DETERMINATION OF ARSENIC.

Element	As
Effective calibration range	0-150 ng/ml
Instrumental Data	
source	electrodeless discharge lamp
wavelength	195.4 nm
slit	4
sample volume	20 µl
purge gas	N_2
gas interrupt	auto
drying time temp.	20 sec.
temp.	100 °C
charring time	30 sec.
temp.	1200 °C
atomizing time	8 sec.
temp.	2500 °C

APPENDIX C

ANALYTICAL PROCEDURE FOR DETERMINATION OF ATRAZINE

The procedure for analysis of atrazine was adapted from Richard et al. (1975) and involved sorption of the atrazine on XAD-2 resin prior to separation, identification, and quantification.

Petroleum ether, acetonitrile, and ethyl ether of pesticide quality were obtained from Burdick and Jackson. XAD-2 macro-reticular resin (Rohm and Haas) was purified by sequential Soxhlet extraction with methanol and acetonitrile. The resin was passed through a sieve and divided into three portions: > 30 mesh, 30-60 mesh, and < 60 mesh. It was then stored under methanol in glass-stoppered bottles.

Gas chromatography was performed with a Fisher-Victoreen Series 4406 gas chromatograph equipped with a Ni^{63} EC detector, the column (170 cm x 0.2 cm i.d.) was a 1.5% OV-17/1.95% QF-1 on Chromasorb W(HP) (80/100).

To perform the analysis, five columns were prepared using $\sim$ 5 ml each of 30/60 mesh XAD-2 resin. The methanol in which the XAD-2 was stored was drained off, and each column was washed with 50 ml of ether, then equilibrated with deionized water by running 100 ml of deionized water through the column. The stopcock was closed when the deionized water was at the top of the column.

An aliquot (5 ml) of sample was placed on the top of each column. The sample was allowed to drain to the top of the column. Deionized water (5 ml) was placed on the column to wash the particulate sticking to the side of the glass into the column; it was allowed to drain completely, then diethyl ether (15 ml) was added to the resin. About 5 ml was allowed to flow through the resin and collect in a separatory funnel (60 ml). Then the stopcock was closed for 15-30 min after which the remaining 10 ml of ether was collected in the funnel. This elution procedure was repeated with a second 15 ml portion of ether which was combined with the first. The water layer was drained from the funnel and removal of the final traces of water in the eluate was accomplished by adding petroleum ether (10-15 ml) and anhydrous Na_2SO_4. The resulting mixture was shaken ~ 30 sec and the liquid extract was transferred quantiatively to a test tube. The extract was concentrated to 1 ml by a blowdown under a gentle stream of N_2.

Gas chromatography was performed with a Fisher-Victoreen Series 4400 gas chromatograph equipped with a Ni^{63} EC or tritium EC detector. The column (170 cm x 0.2 cm i.d.) was a 1.5% OV-17/1.95% QF-1 on Chromasorb W(HP) (80/100). Carrier gas was N_2 at 20 ml/min and the sample injection amount was 1 μl.

APPENDIX D

ANALYTICAL PROCEDURES FOR DETERMINATION OF ORYZALIN

Ultraviolet-visible spectra of the samples before and after various treatments were measured on a Perkin Elmer Model 402 ultraviolet-visible spectrophotometer. Dilutions were made as necessary to maintain absorbances less than 2.0 for the region of 330 to 600 nm. This permitted the evaluation of the removal of colored components. The absorbance maximum for oryzalin is at 378 nm; however, the wastewaters contain other colored materials. The presence of other colored materials was further confirmed in some cases by thin layer chromatography. Silica gel thin layers (Brinkmann) were washed with methanol and activated at 110°C. After spotting the samples, the plates were developed in hexane: acetone 55:45 (v/v). Scanning densitometry may be used to quantitate oryzalin down to ∿ 500 ppb in water; however, this was not sensitive enough to detect oryzalin in wastewater samples.

The method of Sieck *et al*. (1976) was used for oryzalin determination. In this method the sample was cleaned by a liquid-liquid partition and column chromatography on alumina using 95:5, benzene:ethylacetate, as the eluent. The purified oryzalin was then derivatized with methyliodide to give the N,N-dimethyl derivative. The quantitation was made by GC/ECD on a column packed with 5% SE 30 on Supelcoport. Detection limits of ∿ 2 ppb were obtained with this method, but no oryzalin itself was detected in the wastewaters although there were very high levels of closely related colored compounds.

APPENDIX E

ANALYTICAL PROCEDURE FOR DETERMINATION OF MSMA

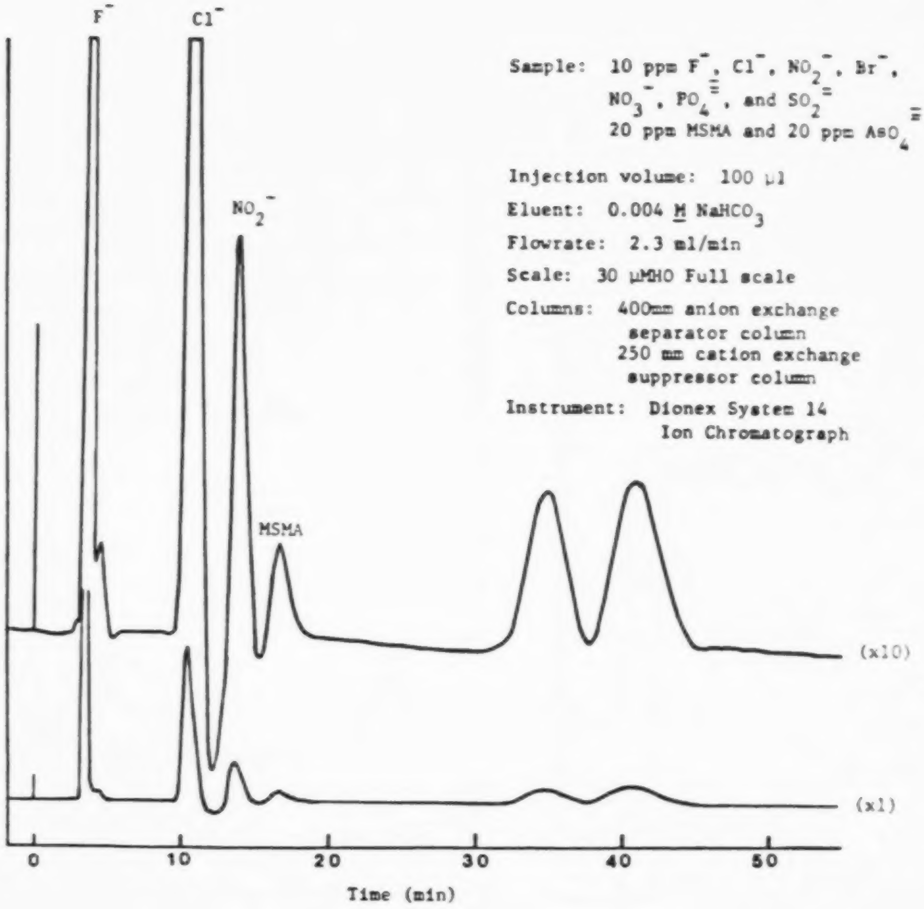
Currently available analytical methodology for MSMA is deficient on several counts for the analysis of this compound if other arsenic compounds are present. A few methods based upon the formation of volatile derivatives and subsequent gas chromatographic analysis are available (Johnson *et al*., 1973; Lodmell, 1973; Salmi *et al*., 1946; Talmi and Bostick, 1975; and Talmi and Feldman, 1975). Problems exist with derivitization reactions which tend to give artifacts and produce extremely toxic volatile products. With these gas chromatographic methods special spectrophotometric detectors such as microwave emission spectrometric detectors or flame spectrometric detectors are utilized. These drawbacks led us to attempt liquid phase analysis. The range of pK's of the various probable arsenic compounds (*i.e*., arsenic acid, methylarsenic acid and dimethylarsenic acid) indicated separation by ion exchange chromatography should be possible if a sensitive detection system were available. The recently developed technique of ion chromatography (Small *et al*., 1975, Sawicki *et al*., 1978) was ideally suited to the problem. The basic principle of this technique is the use of a low capacity, high resolution analytical ion exchange column and a high capacity, low volume suppressor column, of the opposite type from the analytical column, *i.e*., a cationic suppressor column with an anionic analytical column. A buffer is then chosen which results in a nonionic species when neutralized by the suppressor column; a microflow conductivity detector is used to detect ionic species remaining. An example is HCO_3/CO_3 used as eluent. The neutralization of these ions results in H_2CO_3 which yields a very low conductivity background.

Initial experiments revealed that methylarsenic acid and arsenic acid could be readily detected and were well separated from each other when using a 500 mm anion exchange analytical column and a 250 mm cation suppressor column. The eluent was 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Under these conditions nitrite and nitrate interfered. Since methylarsenic acid was the species of interest here, the chromatographic conditions were optimized for its resolution from nitrite at the expense of arsenic acid. A sample chromatogram is shown in Figure E-1. Analysis of the untreated wastewater samples produced the chromatogram in Figure E-2. Only small amounts of fluoride or chloride were present in addition to the methylarsenic acid. The manufacturing wastewater could be injected directly into the instrument with no preparation other than filtering through a 5 μm membrane filter (Millipore Corp.). The effluents from evaluation of activated carbon for the removal of MSMA were analyzed in the same way.

Influents and effluents from the activated sludge units fed 10% MSMA wastewater could not be injected directly since (1) the ten-fold dilution placed the final MSMA concentration at or below the limit of detection and (2) the domestic sewage contained such high anion concentrations that simple concentration steps were not effective. With a 11.6 mg/l MSMA concentration (6.2 mg/l As) in the filtered wastewater a 10-fold dilution would give a 1.2 mg/l final concentration, approaching the limit of detection (0.5 mg/l MSMA). Freeze-drying the sample (100 ml) and redissolving it in 10 ml was effective in concentrating the sample; however, the other anions were also concentrated and the ion chromatogram which resulted is shown in Figure E-3.

The principal interferent was chloride ion and the following steps were added to the procedure for removal of excessive chloride. A cation exchange resin (Bio-Rad AG 50W-X8, 100/200 mesh) was converted to the Ag^+ form with 1M $AgNO_3$ and washed with deionized water until no Ag could be detected in the wash water. Columns were prepared in thistle tubes with a tip drawn in the end and a glass wool plug was used to retain the resin. The resin was protected from light by wrapping with opaque material. The columns were about 2 mm (id) and 6 cm long. Each freeze dried sample (100 ml initial volume) was taken up in 8 ml of deionized water and transferred to the columns. The effluents were collected in 10 ml volumetric flasks and diluted to the mark after the column cleanup. In most cases, a clear chloride-free sample was obtained and precautionary filtration through a 5 μm membrane filter was all that was required to obtain ion chromatograms such as those shown in Figures E-4 and E-5.

Colored samples were obtained from the sludge samples, apparently due to the formation of a silver chloride suspension. This suspension could effectively be removed by ultrafiltration. To eliminate this interference, therefore, activated sludge samples from the test units were treated in the same manner as the influent and effluent samples, with the following exceptions: (1) filtration through a Whatman No. 1 filter before removal of chloride; (2) filtration through a filter of nominal porosity of 10,000 molecular weight (Diaflow UM-10 filter) prior to ion chromatography.



Sample: 10 ppm F^-, Cl^-, NO_2^-, Br^-,
NO_3^-, $PO_4^{\equiv}$, and $SO_2^{=}$
20 ppm MSMA and 20 ppm $AsO_4^{\equiv}$

Injection volume: 100 µl

Eluent: 0.004 M $NaHCO_3$

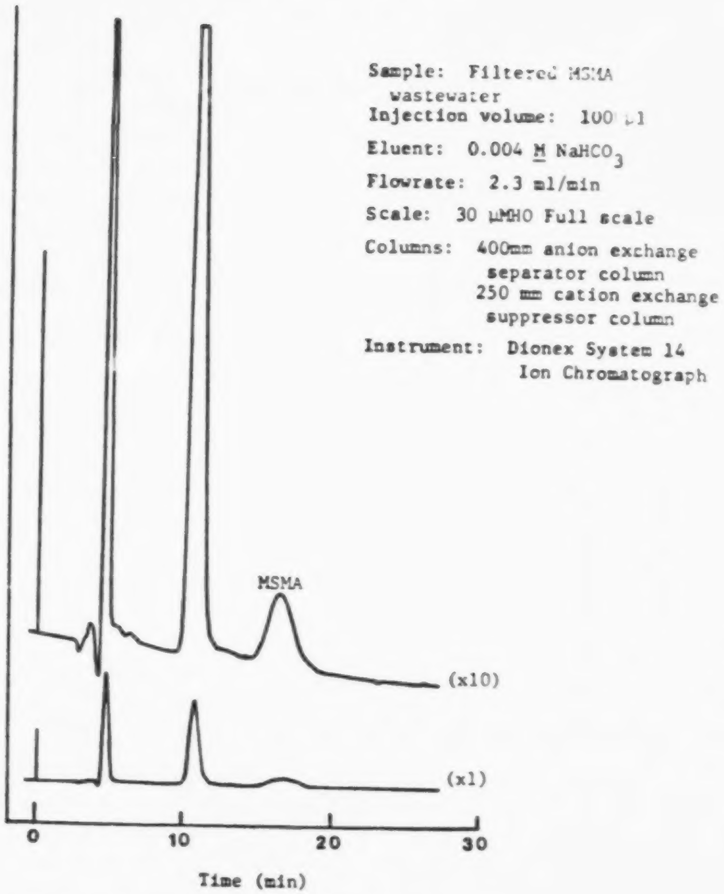
Flowrate: 2.3 ml/min

Scale: 30 µMHO Full scale

Columns: 400mm anion exchange
separator column
250 mm cation exchange
suppressor column

Instrument: Dionex System 14
Ion Chromatograph

Figure E-1. Ion chromatogram of standard anion mixture.



Sample: Filtered MSMA wastewater
Injection volume: 100 µl
Eluent: 0.004 $\underline{M}$ $NaHCO_3$
Flowrate: 2.3 ml/min
Scale: 30 µMHO Full scale
Columns: 400mm anion exchange separator column
250 mm cation exchange suppressor column
Instrument: Dionex System 14 Ion Chromatograph

Figure E-2. Ion chromatogram of MSMA wastewater.

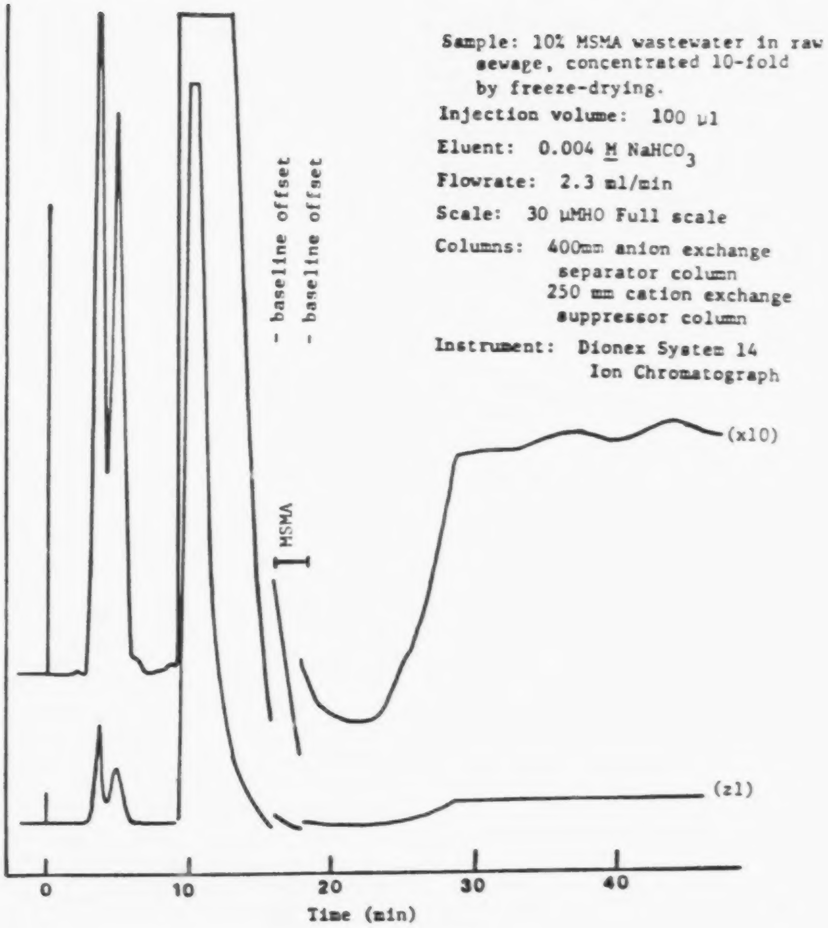
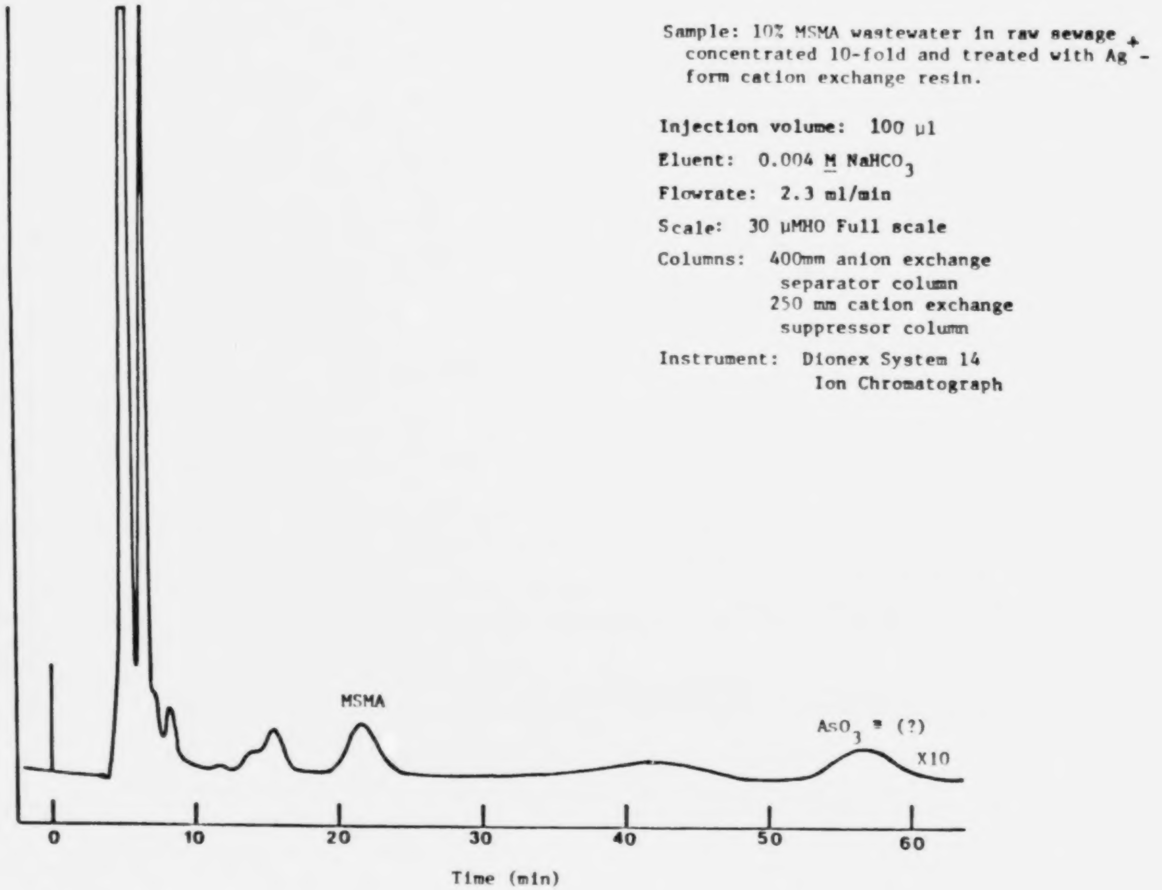


Figure E-3. Ion chromatogram of MSMA wastewater diluted with sewage.



Sample: 10% MSMA wastewater in raw sewage concentrated 10-fold and treated with Ag^+-form cation exchange resin.

Injection volume: 100 µl

Eluent: 0.004 M $NaHCO_3$

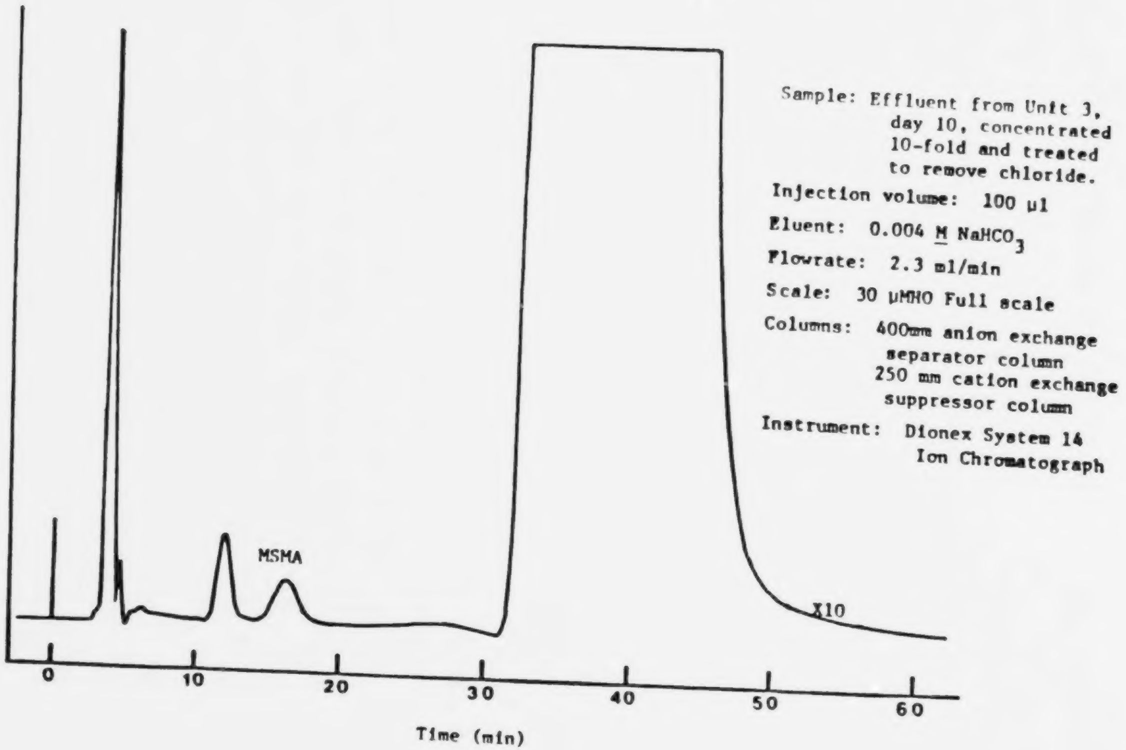
Flowrate: 2.3 ml/min

Scale: 30 µMHO Full scale

Columns: 400mm anion exchange separator column
250 mm cation exchange suppressor column

Instrument: Dionex System 14 Ion Chromatograph

Figure E-4. Ion chromatogram of MSMA wastewater in sewage - after chloride removal.



Sample: Effluent from Unit 3, day 10, concentrated 10-fold and treated to remove chloride.

Injection volume: 100 µl

Eluent: 0.004 M $NaHCO_3$

Flowrate: 2.3 ml/min

Scale: 30 µMHO Full scale

Columns: 400mm anion exchange separator column
250 mm cation exchange suppressor column

Instrument: Dionex System 14 Ion Chromatograph

Figure E-5.. Ion chromatogram of effluent from activated sludge treatment of MSMA wastewater.

APPENDIX F

ANALYTICAL PROCEDURES FOR MANEB AND ITS BREAKDOWN PRODUCTS

Maneb--

The procedure for maneb determinations was adapted from McLeod and McCully (1969) and involves reduction of maneb to carbon disulfide (CS_2) using stannous ion, followed by measurement of CS_2 by GC/ECD. This method does not provide information on speciation of the dithiocarbamate breakdown products and is sensitive to the disulfide and monosulfide cyclic thiocarbamates as well as the metal complex. The method is insensitive to ethylthiourea, the end product of maneb oxidation.

The maneb reference standard (98% pure) was obtained from the Quality Assurance Section, Environmental Toxicology Division of EPA, Research Triangle Park, NC. The CS_2 standard (certified ACS) was obtained from Fisher Scientific Co. The stannous chloride reagent was prepared fresh daily from the ACS grade chemical (Fisher Chemical Co.) by dissolving 1.5 g in 100 ml of 6 M HCl. Standards were prepared by weighing out the appropriate amount of maneb and placing it into a 50 ml narrow mouth amber bottle along with 1 ml H_2O and 9 ml of the stannous chloride reagent. Bottles were closed with septum caps. Samples were prepared in the same way, using 1 ml of the sample or a dilution. Samples and standards were then shaken for at least 0.5 hr. at 65°C in a water bath. For analysis, an appropriate amount of headspace was withdrawn with a gas-tight syringe (Pressure-Lok, Series A-2, Precision Sampling Corporation) and analyzed by GC/ECD.

Gas chromatography was performed with a Fisher-Victoreen Series 4400 gas chromatograph equipped with a tritium scandide detector. The column (170 x 0.2 cm) was Pyrex glass packed with 0.2% Carbowax 1500 on 60/80 Carbopack C, with an anhydrous sodium sulfate plug (2.5 cm long) preceding the packing. The oven and injection port were at ambient temperature and the detector was at 300°C. Nitrogen gas was used as a carrier (at 15 ml/min) and as makeup gas (10 ml/min). Sample injection size was 0.025-0.5 ml.

A standard curve indicated a linear response over the range of 2-130 mg/l of maneb.

Analysis of Maneb in Manufacturing Wastewaters--

Wastewaters, both filtered and unfiltered, were analyzed for maneb. In actual wastewaters there appeared to be a solubility limit of maneb and its breakdown products which generate CS_2 under conditions of acid hydrolysis. One of the wastewaters contained an appreciable amount of undissolved solids and an extremely high concentration of maneb and related compounds was detected, whereas the concentration in filtered samples was 40-46 mg/l for all wastewaters. It is presumed that the solids are undissolved dithiocarbamates.

In order to gain some information on the possible role of dissolved CS_2 on the analytical results, a series of experiments was performed in which the amount of CS_2 generated was monitored for maneb and a maneb wastewater as a function of the presence or absence of the acid hydrolysis reagent and/or shaking at 65°C. Ninety μg of maneb was placed in each of three 50 ml narrow-mouth amber bottles. To the first was added 1 ml of H_2O. The bottle was stoppered and allowed to remain at room temperature for 0.5 hr. To the second was added 10 ml of H_2O, and the bottle was stoppered and shaken at 65°C for 0.5 hr. To the third was added one ml of H_2O and 9 ml of $SnCl_2$-acid reagent; it was then stoppered and shaken at 65°C for 0.5 hr. One ml of unfiltered maneb wastewater was placed in each of four 50-ml narrow-mouth amber bottles. The first bottle was allowed to stand at room temperature for 0.5 hr, while the other three were shaken for 0.5 hr at 65°C. The latter three bottles contained respectively:

(1) 1 ml wastewater alone

(2) 1 ml wastewater + 9 ml H_2O

(3) 1 ml wastewater + 9 ml of $SnCl_2$-acid reagent.

Results were as follows:

Sample	Normalized Peak Areas
Maneb Standards	
90 ppm maneb, 1 ml H_2O, unheated	2.99
90 ppm maneb, 10 ml H_2O, heated	4.64
90 ppm maneb, 1 ml H_2O, 9 ml $SnCl_2$-acid reagent, heated	18.50
Wastewater, unfiltered	
1 ml wastewater, unheated	3.61
1 ml wastewater, heated	4.87
1 ml wastewater + 9 ml H_2O, heated	4.52
1 ml wastewater + 9 ml $SnCl_2$-acid reagent, heated	6.70

Apparently, there is an equilibrium which is temperature dependent established between the various breakdown products of maneb including CS_2. Only a small fraction of the CS_2 generated is to be found in the head space, while most remains dissolved. The solubility of CS_2 in water is 2.2 mg/ml at 22°C and 1.4 mg/ml at 50°C (from CRC Handbook of Chemistry and Physics, 53rd Edition).

It is not feasible to measure the residual CS_2 in the sample before acid hydrolysis, since in the presence of only H_2O some hydrolysis does occur, and the amount of CS_2 present in the head space is affected by the change in equilibrium created by heating the sample to 65°C.

Maneb Breakdown Products--

Maneb breakdown products were determined by the method of Czeglédi-Jankó (1967). The procedure involves chloroform-ethanol extraction of the dry maneb sample followed by thin layer chromatography of the extract. No standards are commercially available for ethylene dithiocarbamate disulfide (ETD) or monosulfide (ETM). The ETU standard was 97% pure and was obtained from Aldrich Chemical Company.

Solid samples were weighed to yield approximately 0.5 g of maneb; unfiltered liquid samples were mixed and a 200 ml aliquot freeze-dried before the extraction. The commercial maneb was extracted with 5 ml of 1:1 chloroform: ethanol mixture. The wastewater samples from plants A and B were extracted with 20 and 50 ml chloroform:methanol (1:1) respectively. The adjustment of volume was based upon the amount of residue. Aliquots of 10 to 25 µl of these extracts were spotted on Silica Gel G TLC plates (Brinkman) and developed with chloroform: butanol-methanol-water (100:5:-1:0.5). After evaporation of the solvents, the TLC plates were placed in a chamber saturated with iodine vapor for about 10 min. The color developed was preserved by covering with a glass plate. Photographs of these plates are shown in Figures F-1 and F-2 with an ethylene thiourea (ETU) standard. Although no standards of ETD or ETM were available, comparison of our plates with those published by Czeglédi-Jankó (1967) indicate spots having the same R_f relative to ETU. Areas corresponding to ETU showed extensive concentration reversal after the initial 10 min exposure to iodine. However, this exposure gave the best visualization of the other breakdown products. Chromatograms of the plates were obtained via scanning spectrodensitometer (Schoeffel SD 3300, transmission mode, 680 nm wavelength, 2 mm slits).

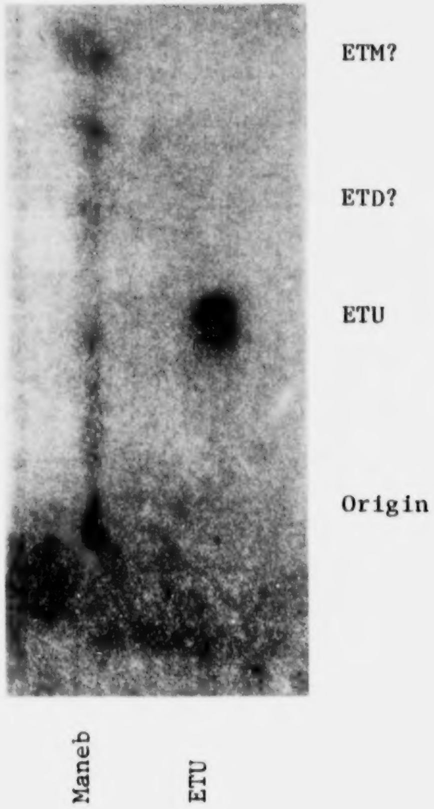

ETM?
ETD?
ETU
Origin
Maneb
ETU

Figure F-1. Thin-layer chromatogram of the extract of commercial formulated maneb and ETU.

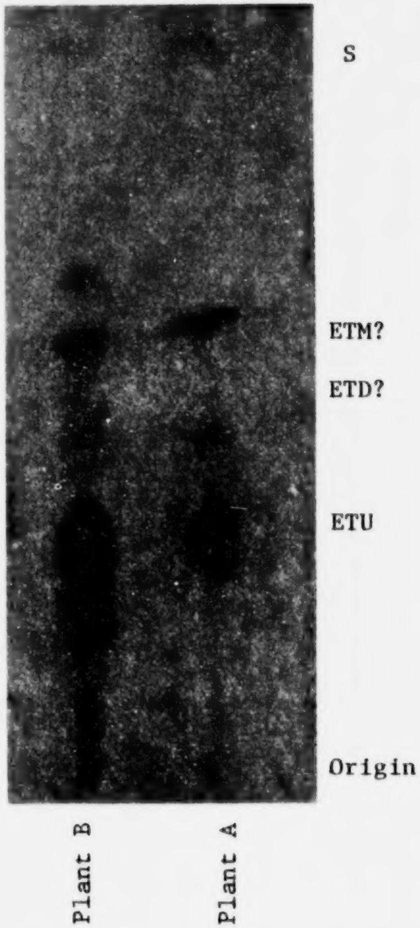

S
ETM?
ETD?
ETU
Origin
Plant B
Plant A

Figure F-2. Thin-layer chromatogram of the extracts of Plant A (right) and Plant B (left) wastewaters.

APPENDIX G

PROCEDURE FOR CONDUCTING ACTIVATED CARBON TREATABILITY TESTS

Liquid Adsorption Isotherm Tests

Sources of Carbon--

The following types of carbon were used in preliminary liquid adsorption isotherm tests:

LCL	Union Carbide
LCK	Union Carbide
Nuchar SA	Westvaco
Nuchar WV-L	"
Nuchar WV-G	"
Filtrasorb 400	Calgon Corporation
Hydrodarco	ICI Americas, Inc.

Carbons which were not received in powder or pulverized form were crushed and passed through a 325-mesh screen as recommended for isotherm testing (Metcalf & Eddy, Inc., 1972).

Procedure--

The procedure for isotherm tests was modified from Metcalf and Eddy, Inc. (1972). Aliquots (100 ml) of the filtered (Whatman 2V) wastewater were placed in flasks and dosed with the carbon to give a final carbon concentration of 0, 400, 800, 1600, or 20,000 mg/l. They were placed on a shaker and agitated for 2 hr at 22-24 C. Carbon was removed by passage through a glass-fiber filter and residual pesticide levels were measured.

GAC Column Tests

Calgon Filtrasorb 400 was chosen for large-scale tests. It was dried ($\geq$ 2 hr at 150 C) to constant weight before use. It was slurried in hot water to expel trapped air, then added to the column in small increments, keeping a thin layer of supernatant liquid present at all times. Wastewater was pumped (Masterflex) pump onto the top of the column at a rate giving a flow of ~ 0.5 gpm/ft^2. This is recommended as a good starting rate in pilot tests but is lower than is generally used in practice (Metcalf and Eddy, 1972). Because of the limited amount of wastewater available, it was chosen for these studies. Depending on sorptive capacity of the carbon for the specific wastewater, a short (15.2 cm height x 2.2 cm i.d.) or long (120 cm height x 2.5 cm i.d.) glass column was used. With the exception of the MSMA wastewater, which was free of suspended solids, the wastewaters were filtered (Whatman 2V, medium porosity) prior to GAC column treatment. In each run, an initial void volume was collected and discarded before collection of fractions for analysis.

APPENDIX H

PROCEDURES FOR CONDUCTING ACTIVATED SLUDGE TREATABILITY TESTS

For biological treatability studies the miniature complete mix continuous activated sludge unit designed by Swisher (1970) was employed (Figure H-1). This unit has an aerator capacity of 0.3 l and a settler capacity of 0.075 l. The unit is completely made of glass, avoiding the possibility of contamination by organics leaching from the container. Feed to the units was supplied continuously through Teflon tubing by gravity feed or by peristaitic pumps to give a nominal retention time of 8 hr.

A battery of 6 units was run in each test. The units were started with activated sludge from the Hope Valley Treatment Plant, Durham, NC, which treats municipal wastewater. The units were then fed from a reservoir of primary sewage from this plant. When a steady-state condition was reached, as indicated by consistent effluent quality in terms of COD and by similar mixed liquid suspended solids levels, the feed to the test units was spiked with pesticide wastewater. Control units were fed only primary sewage.

In most cases the pesticide spiked wastewater feeds were prepared by adding pesticide wastewater to the primary sewage to make a final mixture of 10% pesticide wastewater/90% primary sewage. After thorough mixing, the mixture was allowed to settle for ~ 120 min to simulate primary settling. In some cases, depending on toxicity of the pesticide wastewater, higher or lower concentrations were employed.

Routine determinations were made of dissolved oxygen, pH, mixed liquor suspended solids, COD, and pesticide. Dissolved oxygen was determined with an oxygen probe (Yellow Springs Instrument Co.).

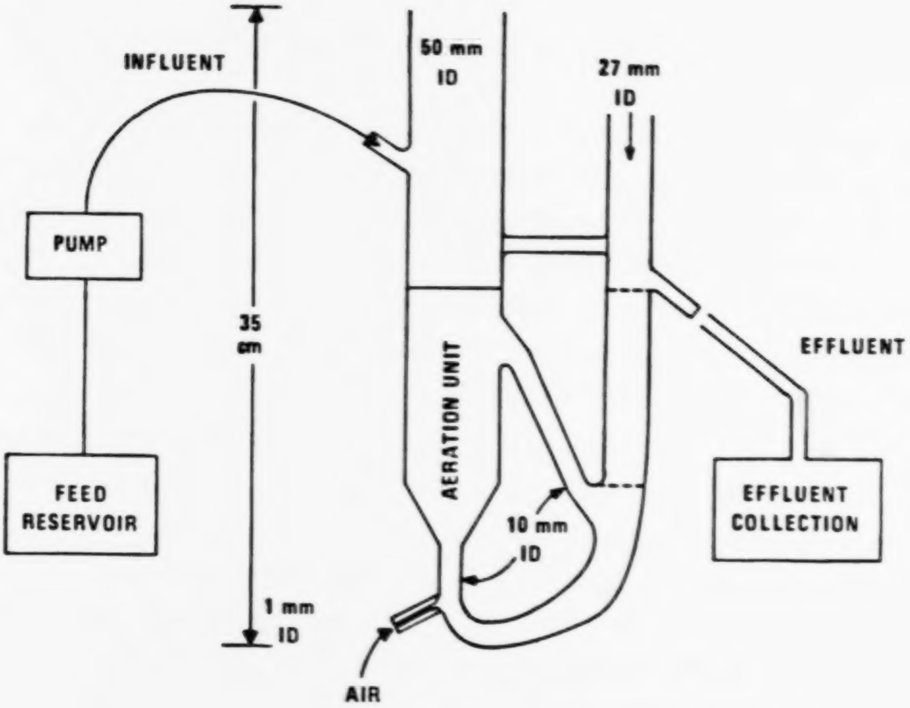

INFLUENT
50 mm
ID
27 mm
ID
PUMP
35
cm
AERATION UNIT
EFFLUENT
FEED
RESERVOIR
10 mm
ID
EFFLUENT
COLLECTION
1 mm
ID
AIR

Figure H-1. Diagram of activated sludge pilot unit.

APPENDIX I

PROCEDURES FOR ALGAL ASSAY TESTS

Algal bioassays were conducted according to the freshwater algal assay procedure: bottle test, according to the procedure described in the IERL-RTP Procedure Manual: Level I Environmental Assessment Biological Tests for Pilot Studies (Duke *et al.*, 1977; APHA *et al.*, 1976). The test alga was *Selenastrum capricornutum* Printz, obtained from the National Eutrophication Research Program, EPA, Corvallis, Ore. This test was designed to measure algal response to changes in nutrient concentrations and to determine toxicity or inhibition.

Wastewaters to be tested were filter sterilized through a sterile prewashed membrane filter (Millipore Filter, 0.45 µm pore size). Serial dilutions were then made in sterile algal media to give the appropriate final concentration. Sufficient inoculum was added to produce an initial cell concentration of 10^3 cells/ml.

In each set of experiments, algal growth in the presence of a series of concentrations of the wastewater as added to the nutrient medium was compared to that in the nutrient medium alone. Growth was determined by direct counts (see below) of the algae during the 10-14 day incubation period. Effect of the wastewater on algal growth was determined in terms of the effect on the growth rate and of the effect on the cell yield. Direct cell counts were performed (I) visually or (II) by an automated procedure. Direct, visual counting with a hemacytometer and microscope was the basic cell counting technique employed in the algal bioassay. Utilizing a hand counter, the algae in 5 squares (4 corners and center) in a ruled 0.1 mm square divided into 25 squares were counted. This number was multiplied by 5 to give the total cells in the 0.1 mm square. Multiplying this number by 10 gave the total cells in a mm^3 and further multiplication by 10^3 gave the number of cells per ml. The automated method of cell counting followed the same preparation procedure as above, however, an automatic cell counter was incorporated. A television camera (Fisher auxiliary camera, 7-909-15) viewed the algal cells through the photographic tube of a microscope, allowing for rapid cell counts following the pattern as described in Method I.

The tests were conducted in water bath shakers at 24 ± 2 C and approximately 110 oscillations per minute with constant white fluorescent lighting at 4300 lux. Test containers were 250 ml Erlenmeyer Pyrex flasks containing 60 ml of test medium and covered with an inverted Pyrex beaker.

Initially, a series of 10-fold dilutions of pesticide wastewaters was tested (generally 10^{-1} to 10^{-5}) to determine the approximate toxic range. Further tests were conducted at concentrations based on progressive bisection of intervals on a logarithmic scale in order to more precisely define that concentration producing 50% inhibition of growth (EC_{50}).

An alternate method of expressing inhibitory or stimulatory effects was that recommended by Miller *et al*. (1978), *i.e.*, as the percent growth inhibition (I) or stimulation (S), as compared to growth in a control culture without the test materials. These authors suggest that, in general practice, the results be based on the growth at 14 days, *i.e.*, as % I_{14} or % S_{14} at a given concentration of the effluent being tested.

Decreased growth, compared to the control, is evidence of an inhibitory effect. The manner in which the test is conducted does not allow determination of whether this inhibition is temporary (algistatic) or permanent (algicidal). Such a determination would require further testing by subculturing into fresh medium free of the test material.

APPENDIX J

PROCEDURE FOR FISH BIOASSAY TESTS

The fish bioassay procedure chosen was the standard 96-hour static bioassay (APHA, *et al*., 1976; Duke *et al*., 1977). The static method has been criticized as being rather simplistic, and more complex alternate methods have been suggested (Brown, 1973; Cairns, 1969; Eaton, 1973; Peltier, 1978; Scheier and Burton, 1973, Sprague, 1973; Stephen, 1973). However, the relative simplicity and economy of the static method make it the method of choice in initial screening. The test fish was the fathead minnow, *Pimephales promelas*, selected from a list of recommended species prepared by D. I. Mount of the National Water Quality Laboratory (as reported in Cairns, 1969). This species has been widely used in fish bioassay studies and is adaptable to laboratory conditions. Test fish were obtained from Windmill Fish Hatcheries, Kernersville, NC and Kurtz's Fish Hatchery, Elverson, PA. New shipments of fish were routinely exposed on arrival to the broad-spectrum antibiotic tetracycline HCl at a dose of about 13 mg per gallon of water for 24-48 hr. This treatment helps prevent introduction into the stock tank of diseases from fishery stock or from fish damaged in shipment. On evidence of disease in the stock tanks, the tetracycline treatment was repeated. Fish were maintained in 30-gal glass aquaria equipped with devices for aeration, recirculation, and filtration. The water was Durham tapwater treated to remove chlorine and organic carbon by passage through an activated carbon filter (Sears No. 42-3464). The tanks were kept in a room maintained at 24 ± 2 C, with a light cycle of 8-hr dark and 16-hr light.

Small-scale exploratory bioassays were conducted to determine the range of concentrations to be tested in full-scale tests. For these screening tests solutions were prepared as decimal dilutions of the wastewater (such as 0.01, 0.1, 1.0 percent). A test volume of 3 liters and 3 fish per container were used.

Based on results of the screening assays, a full-scale test range was chosen, with the concentrations falling between the highest concentration at which all fish or most of the fish died. In these tests, the LC_{50} was determined by testing a series of concentrations based on progressive bisection of intervals of the logarithmic scale, such as 1.0, 1.8, 3.2, 5.6, and 10.0 percent, multiplied or divided as necessary by any power of 10. These values are evenly spaced when plotted on a logarithmic scale.

In each test series, control tests were conducted concurrently with the experimental dilution water. In the large scale tests, results were considered invalid if more than 10% mortality occurred among the control fish. In the large scale tests, test containers were 5-gal wide-mouth glass jars, 25 cm (d) x 47 cm (h), containing 15 liters of test solution. To test each experimental concentration, 10 fish were used. Fish were not fed for 48 hr prior to testing nor during the tests.

Use of 10 or more test fish per toxicant concentration has been the "usual practice" for short-term static tests according to Standard Methods (APHA et al., 1976). As noted in this document, "a number of factors govern the precision of the results of a bioassay and the arbitrary setting of the number of test organisms will not assure a certain precision for the results." An example is cited of tests with sewage effluent indicating that with 10 fish per toxicant concentration, the 95% confidence interval was within ± 20% of the means while when 20 fish were exposed it was within ± 14% of the mean value.

LC50 values were estimated by interpolation after plotting the data on semilogarithmic coordinate paper with concentrations on the logarithmic and percentage dead on the arithmetic scale, as described in Section 801F.1 (APHA et al., 1976). This method of interpretation has been shown to give values within the precision of the test.

APPENDIX K

FISH AND ALGAL BIOASSAY DATA--ATRAZINE WASTEWATER STUDIES

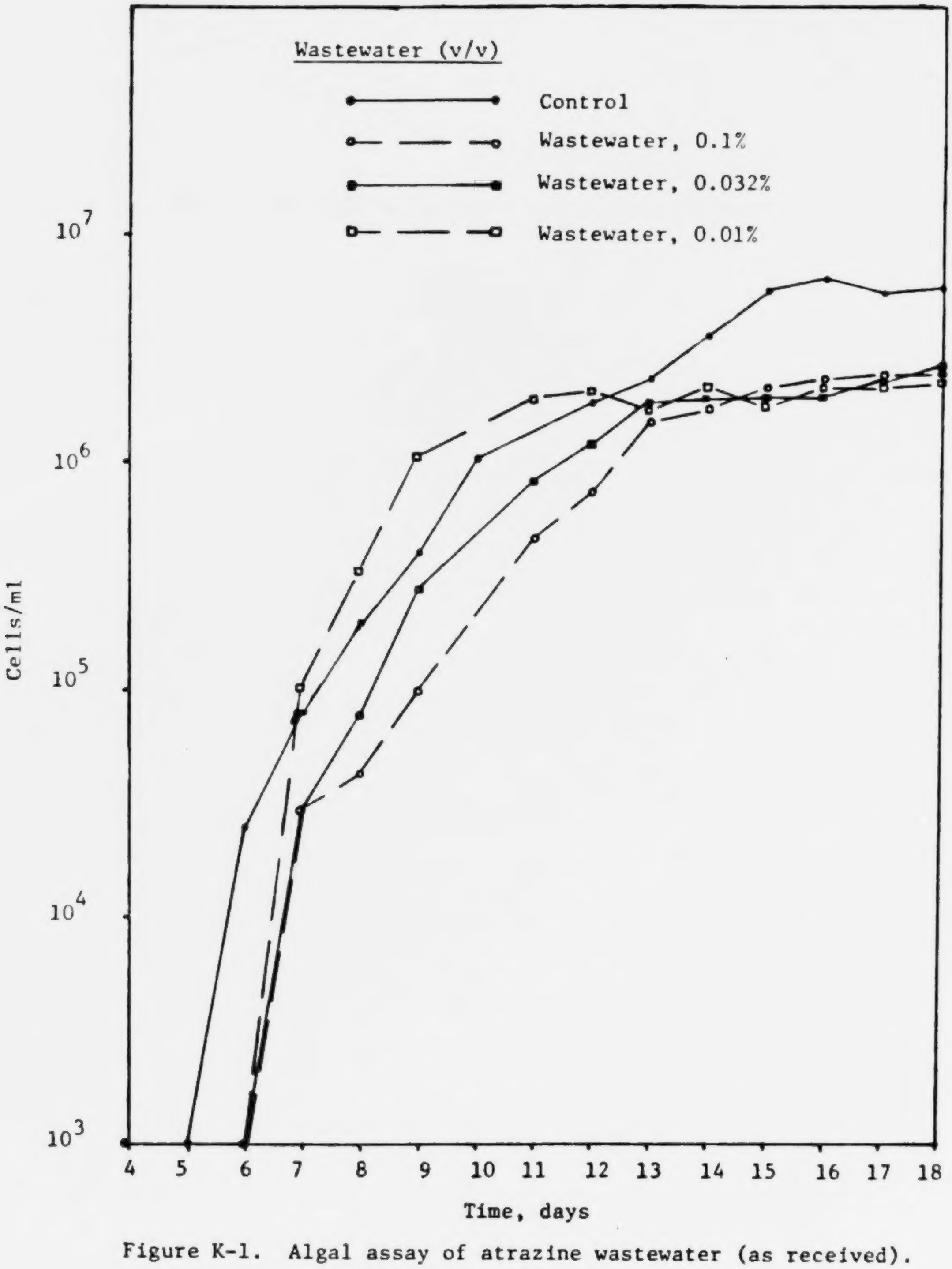


Figure K-1. Algal assay of atrazine wastewater (as received).

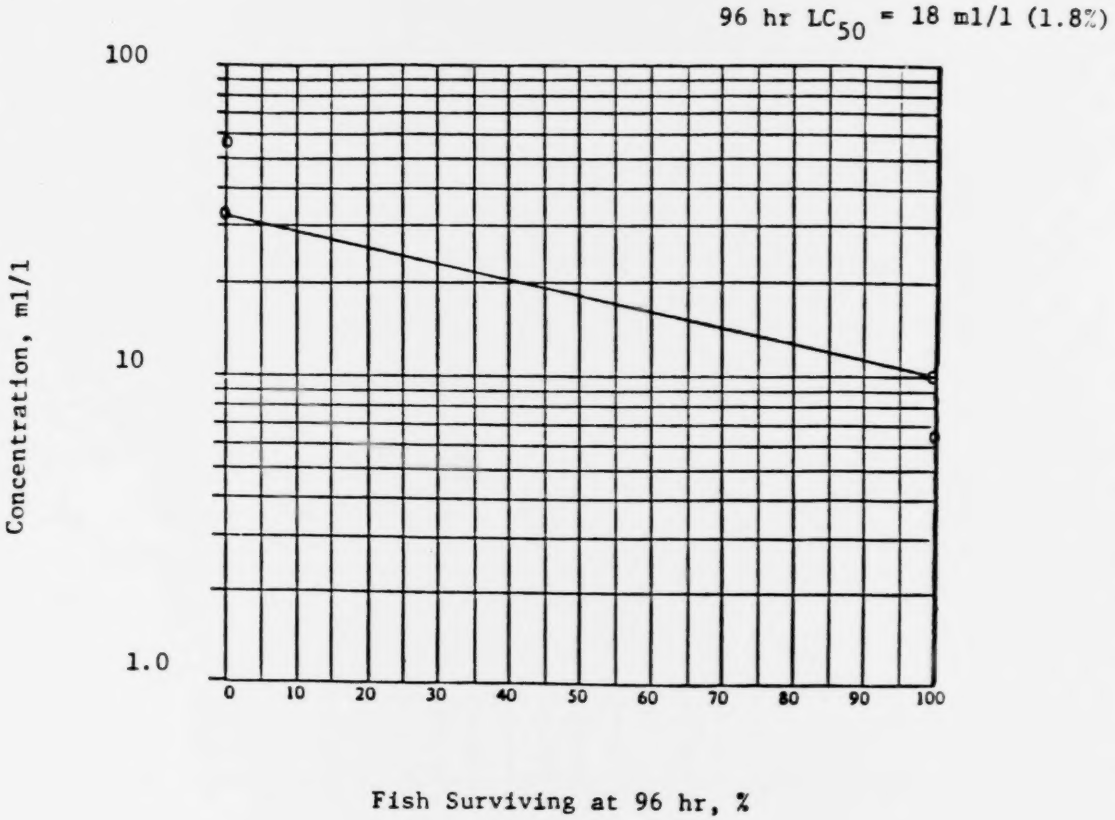


Figure K-2. 96 hr LC_{50} determination: atrazine manufacturing wastewater (as received).

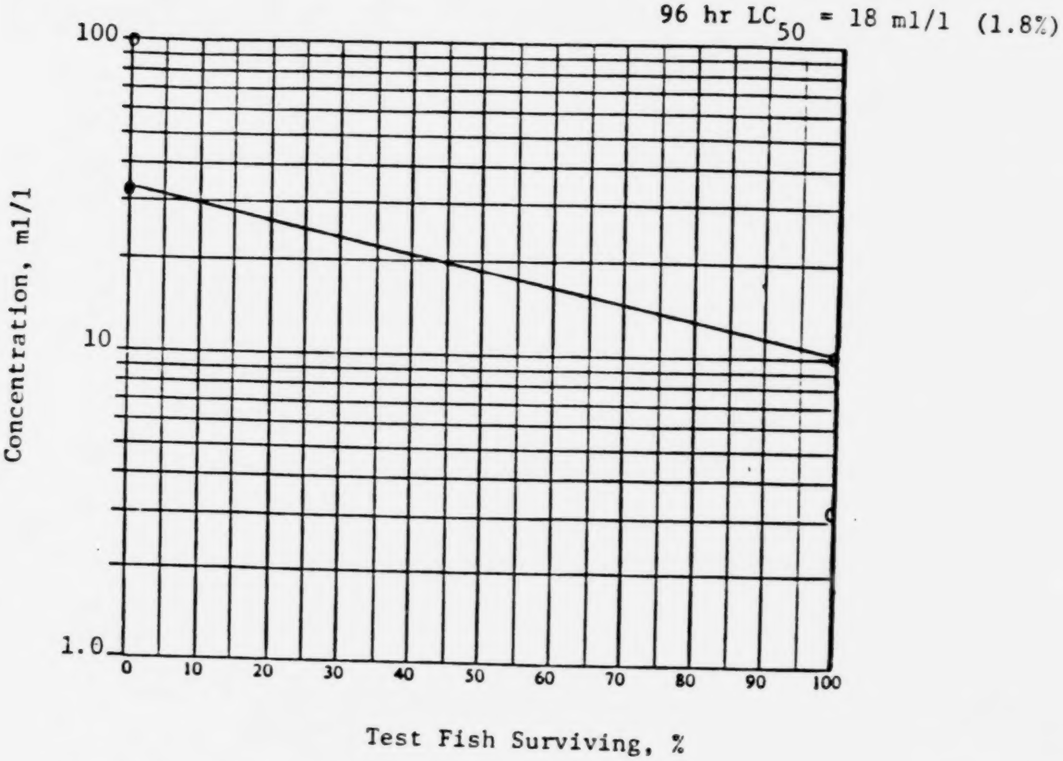


Figure K-3. 96 hr LC_{50} determination: atrazine manufacturing wastewater, filtered, Whatman 2V filter.

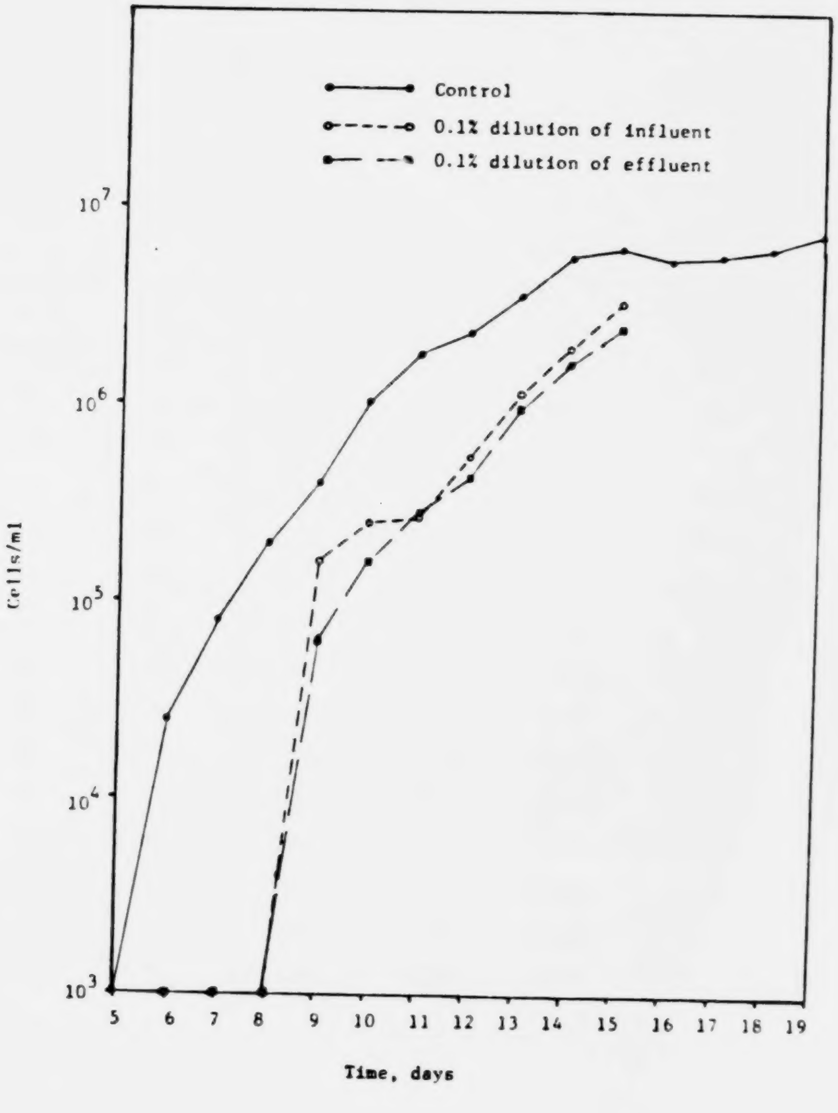


Figure K-4. Algal assay of influent and effluent to activated sludge units fed with atrazine wastewater (16.7%). (Data shown in Table E-4).

Table K-1. EFFECT OF ATRAZINE WASTEWATER (AS RECEIVED) ON ALGAL GROWTH.

	Growth, 10^3 cells/ml				Growth, % of Control		
	Control	Wastewater, % (v/v)			Wastewater, % (v/v)		
Day		0.1	0.032	0.01	0.1	0.032	0.01
0	-	-	-	-	-	-	-
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
6	25	-	-	-	-	-	-
7	80	30	30	205	38	38	256
8	197	43	80	345	22	41	175
9	403	100	290	1107	25	72	275
10	1058	-	-	-	-	-	-
11	1843	470	860	1983	26	47	108
12	2350	750	1260	2133	32	54	91
13	3633	1533	1850	1850	42	51	51
14	5717	1783	2050	2267	31	36	40
15	6383	2167	2025	1850	34	32	29
16	5483	2350	2075	2267	43	38	41
17	5910	2483	2325	2167	42	39	37
18	6325	2467	2700	2400	39	43	38
19	7560	2550	2425	2183	34	32	29
20	6850	2750	2675	1983	40	39	29
21	6342	2183	3025	2400	34	48	38

Table K-2. SCREENING TESTS ON TOXICITY TO FISH OF UNTREATED AND GAC TREATED ATRAZINE WASTEWATER

Sample	Wastewater Concentration, ml/l	pH	No. fish surviving at 96 hr (Initial = 3)
Dilution water control	0	--	3
Filtered wastewater (column feed)	10	7.0	3
	18	7.1	2
	56	7.5	0
	100	7.8	0
GAC column effluent, before breakthrough	10	7.2	3
	18	7.1	2
	56	7.1	3
	100	7.1	2
GAC column effluent, after breakthrough of 1 ppm atrazine	10	7.1	3
	18	7.2	3
	56	8.5	2
	100	8.7	2

Table K-3. EFFECT OF ACTIVATED SLUDGE TREATMENT ON TOXICITY OF ATRAZINE WASTEWATERS TO FISH

Sample	Concentration, ml/l	% Fish Surviving at 96 hr
Control, dilution water	-	100
Control, dilution water	-	100
Primary Sewage Influent	180	100
Primary Sewage Effluent,	100	100
Unit 1	180	100
Primary Sewage + 8.3% Atrazine Wastewater:		
Before Treatment (influent)	32	100
	100	100
After Treatment (effluent)		
Unit 1	32	100
	100	90
Unit 2	32	90
	100	90
Primary Sewage + 16.7% Atrazine Wastewater:		
Before Treatment (influent)	32	100
	100	100
After Treatment (effluent)		
Unit 1	32	80
	100	90
Unit 2	32	90
	100	70

Table K-4. ALGAL ASSAY OF INFLUENT AND EFFLUENT TO ACTIVATED SLUDGE UNITS FED WITH ATRAZINE MANUFACTURING WASTEWATER (16.7%)

	Growth, Percent of Control					
	Influent conc. %(v/v)			Effluent conc., % (v/v)		
Time (days)	10	1.0	0.1	10	1.0	0.1
0	-	-	-	-	-	-
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	-	-	-	-	-	-
9	-	-	40	-	-	16
10	-	-	24	-	-	15
11	-	-	15	-	-	15
12	-	-	24	-	-	18
13	-	-	32	-	-	26
14	-	-	34	-	-	29
15	-	-	52	-	-	29

- = beneath detection limits.

APPENDIX L

FISH AND ALAGAL BIOASSAY DATA--ORYZALIN WASTEWATER STUDIES

Table L-1. TOXICITY OF ORYZALIN AND ORYZALIN WASTEWATERS TO FISH -- SCREENING TESTS

Test Sample	No. fish surviving at 96 hr (Initial = 3)
Oryzalin, unformulated, mg/l	
0.005	3
0.05	3
0.5	3
5.0	3
Oryzalin wastewater (grab sample), % (v/v)	
0.01	2
0.1	0
1.0	0
10.0	0
Oryzalin washwater (grab sample), % (v/v)	
0.01	3
0.1	3
1.0	3
10.0	0
Dilution water control	3

Table L-2. TOXICITY TO FISH OF ORYZALIN MANUFACTURING WASTEWATER

Sample	Concentration, ml/l	Fish Surviving at 96 hr, % (Initial = 10)
Control	0.0	100
Oryzalin wastewater	0.1	80
Oryzalin wastewater	0.18	90
Oryzalin wastewater	0.56	0
Oryzalin wastewater	1.0	0

96 hr LC_{50} = 0.3 ml/l

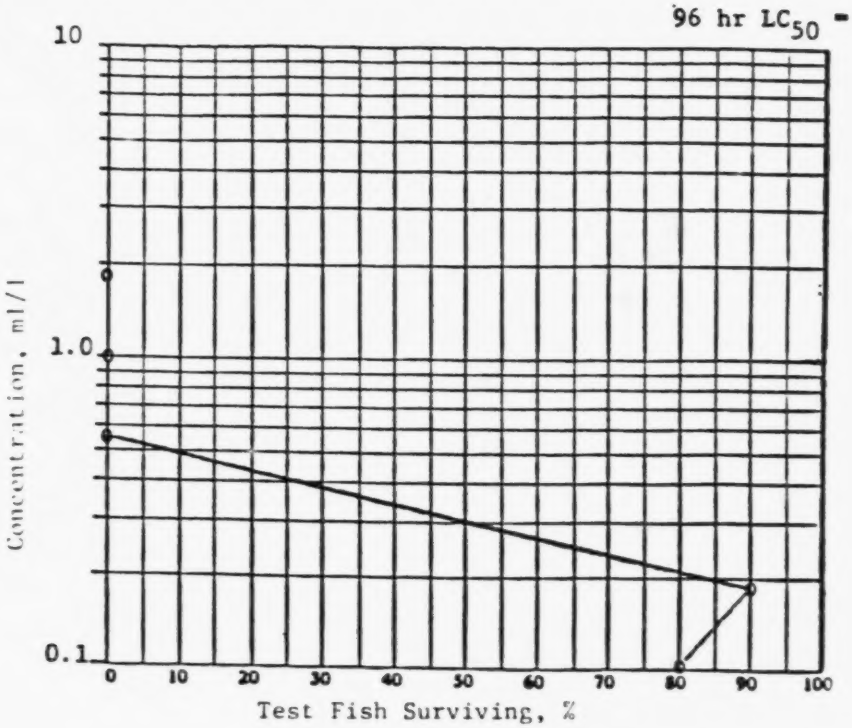


Figure L-1. 96 hr LC_{50} determination: oryzalin manufacturing wastewater.

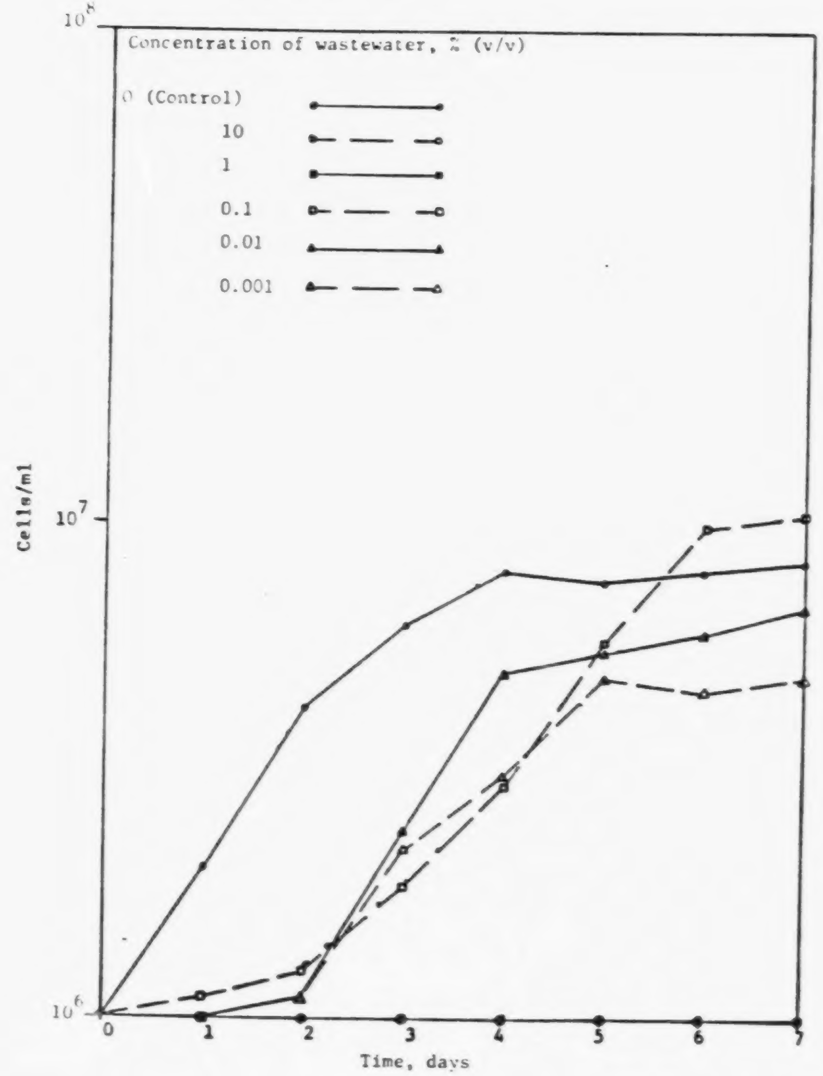


Figure L-2. Algal assay of oryzalin wastewater.

Table L-3. EFFECT OF ORYZALIN WASHWATER ON ALGAL GROWTH, EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

	Growth, Percent of Control, in:				
	Oryzalin Washwater Conc., Percent (v/v)				
Time (days)	10	1.0	0.1	0.01	0.001
1	127	161	150	150	133
2	45	102	74	97	83
3	73	95	110	103	91
4	71	83	95	88	84
5	59	90	97	89	121
6	67	87	79	98	87
7	64	75	88	83	67
8	72	90	96	93	102
9	63	87	99	104	97
10	58	87	98	93	88

Table L-4. EFFECTS OF ORYZALIN WASTEWATER AFTER CARBON TREATMENT ON ALGAL GROWTH EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

Time (days)	Growth, Percent of Control, in: Oryzalin Wastewater Conc., Percent (v/v) 10	1.0	0.1	0.01	0.001
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	-	-	-	-
5	-	-	100	0	0
6	-	-	200	-	100
7	-	-	200	0	100
8	0	200	200	200	200
9	25	13	150	113	128
10					
11	8	0	40	104	50
12	0	0	21	49	28
13	0	3	45	56	64
14	0	54	104	70	82
15	2	1	71	61	83
16	1	1	77	65	68
17	3	2	101	80	108
18	6	2	109	36	82
19	2	2	99	53	77
20	0	0	94	40	66

Table L-5. FISH BIOASSAY OF GAC TREATED ORYZALIN WASTEWATER

Sample	Concentration of ml/l	Wastewater % (v/v)	% Fish Surviving at 96 hrs (Initial = 10)
Control	-		100
Oryzalin Wastewater, GAC Treated	1.0	0.1	0
Oryzalin Wastewater, GAC Treated	1.8	0.18	0
Oryzalin Wastewater, GAC Treated	5.6	0.56	0

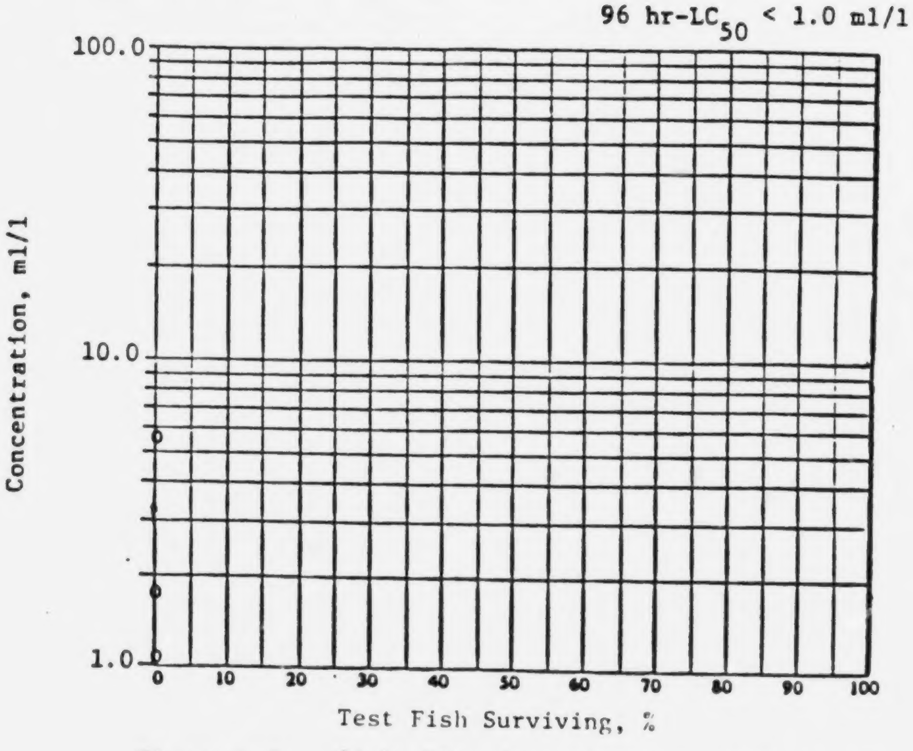


Figure L-3. 96 hr LC_{50} determination: GAC treated oryzalin wastewater.

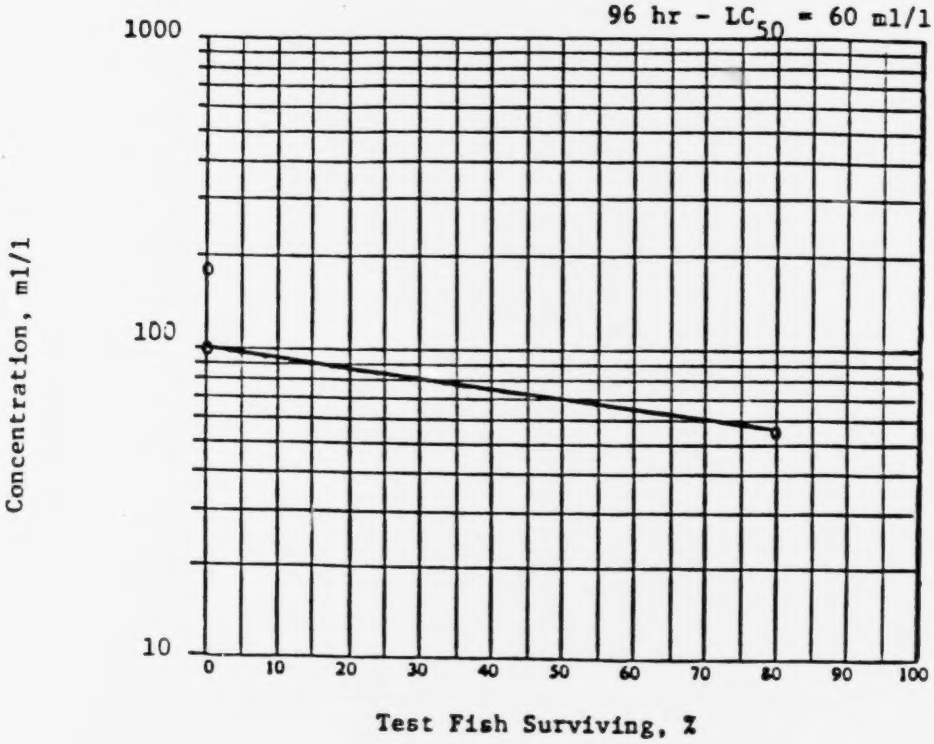


Figure L-4. 96 hr-LC50 determination: untreated domestic wastewater with 1% oryzalin manufacturing wastewater.

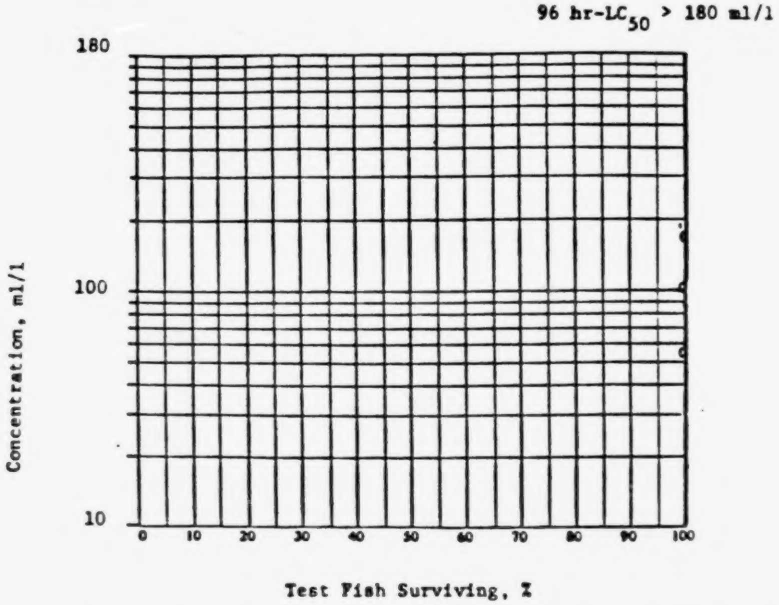


Figure L-5. 96 hr-LC$_{50}$ determination: effluent from activated sludge unit I fed domestic wastewater with 1% oryzalin manufacturing wastewater.

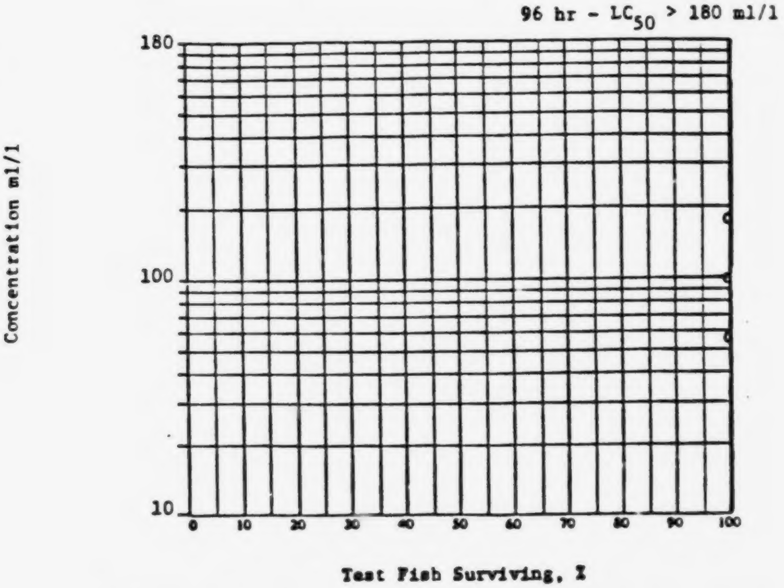


Figure L-6. 96 hr-LC$_{50}$ determination: effluent from activated sludge unit II fed domestic wastewater with 1% oryzalin manufacturing wastewater.

Table L-6. ALGAL ASSAY OF INFLUENT AND EFFLUENT TO ACTIVATED SLUDGE UNITS FED WITH ORYZALIN MANFACTURING WASTEWATER (1%)

Growth, Percent of Control

Time (days)	Influent concn., % (v)			Effluent Concn., % (v/v)		
	10	1.0	0.1	10	1.0	0.1
0	-	-	-	-	-	-
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	50	200	300	-	250	300
8	-	140	180	-	220	80
9	25	138	225	50	325	162
10	9	85	113	5	100	108
11	6	78	100	3	62	47
12	6	86	91	4	80	68
13	7	84	79	4	83	74
14	12	95	82	15	89	84
15	29	112	120	26	114	85

APPENDIX M

FISH AND ALGAL BIOASSAY DATA--MSMA WASTEWATER STUDIES

Table M-1. EFFECTS OF MSMA WASTEWATER ON ALGAL GROWTH (RANGE-FINDING), EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

Time (days)	Growth, Percent of Control, in:				
	MSMA Wastewater Concentration, Percent (v/v)				
	10	1.0	0.1	0.01	0.001
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	-	50	-	50
5	55	44	22	11	0
6					
7	0	400	137	156	100
8	0	124	76	60	94
9	4	94	54	62	56
10	3	64	73	51	43
11					
12	2	49	89	92	102
13	5	40	87	85	80
14	1	64	106	78	128
15	1	134	108	113	130
16	1	46	90	86	76

- = beneath detection limits

Table M-2. EFFECT OF MSMA WASTEWATER ON ALGAL GROWTH (NARROW RANGE), EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

Time (days)	Growth, Percent of Control, in: MSMA Wastewater Concentration, Percent (v/v) 10.0	3.2	1.0
0	-	-	-
1	-	-	-
2	-	-	-
3	-	-	-
4	-	-	-
5	-	-	-
6	-	-	-
7	0	314	200
8	0	475	155
9	0	134	119
10	1	226	179
11	0	172	133
12	0	99	70
13	0	107	67
14	0	95	66
15	0	47	78
16	0	95	62
17	0	98	68

Table M-3. TOXICITY OF MSMA WASTEWATER TO FISH--SCREENING TESTS

Concentration of MSMA Wastewater		Fish Surviving at 96 hr. (initial=3)
ml/l	%	
0	0	3
100	10	2
180	18	0
320	32	0

Table M-4. EFFECT OF AERATION ON TOXICITY TO FISH OF MSMA WASTEWATER--SCREENING TESTS

MSMA Wastewater Concentration		Aeration?	No. Survivors at 72 hr. (Initial=3)
ml/l	%		
180	18	No	0
320	32	No	0
180	18	Yes	2
320	32	Yes	0

Table M-5. EFFECT OF MSMA WASTEWATER AFTER CARBON TREATMENT ON ALGAL GROWTH, EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

	Growth, Percent of Control, in:		
	MSMA Wastewater Concentration, Percent (v/v)		
Time (days)	10.0	3.2	0.1
0	-	-	-
1	-	-	-
2	-	-	-
3	-	-	-
4	-	-	-
5	-	-	-
6	-	-	-
7	-	242	86
8	0	83	424
9	1	31	39
10	0	85	66
11	0	57	72
12	0	97	49
13	0	106	53
14	0	133	48
15	0	140	57
16	0	104	55
17	0	84	56

Table M-6. ALGAL ASSAY OF INFLUENT AND EFFLUENT OF ACTIVATED SLUDGE UNITS FED WITH MSMA MANUFACTURING WASTEWATER (10%)

Growth, Percent of Control, in

Time (days)	Influent conc., % (v/v)		Effluent conc., % (v/v)	
	10	1.0	10	1.0
0	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	-	-	-	-
6	-	-	-	-
7	250	500	750	650
8	360	720	128	920
9	588	938	125	1025
10	206	238	438	282
11	116	136	210	124
12	179	142	182	120
13	205	134	155	95
14	150	130	140	95
15	168	144	175	95

- = beneath detection limits.

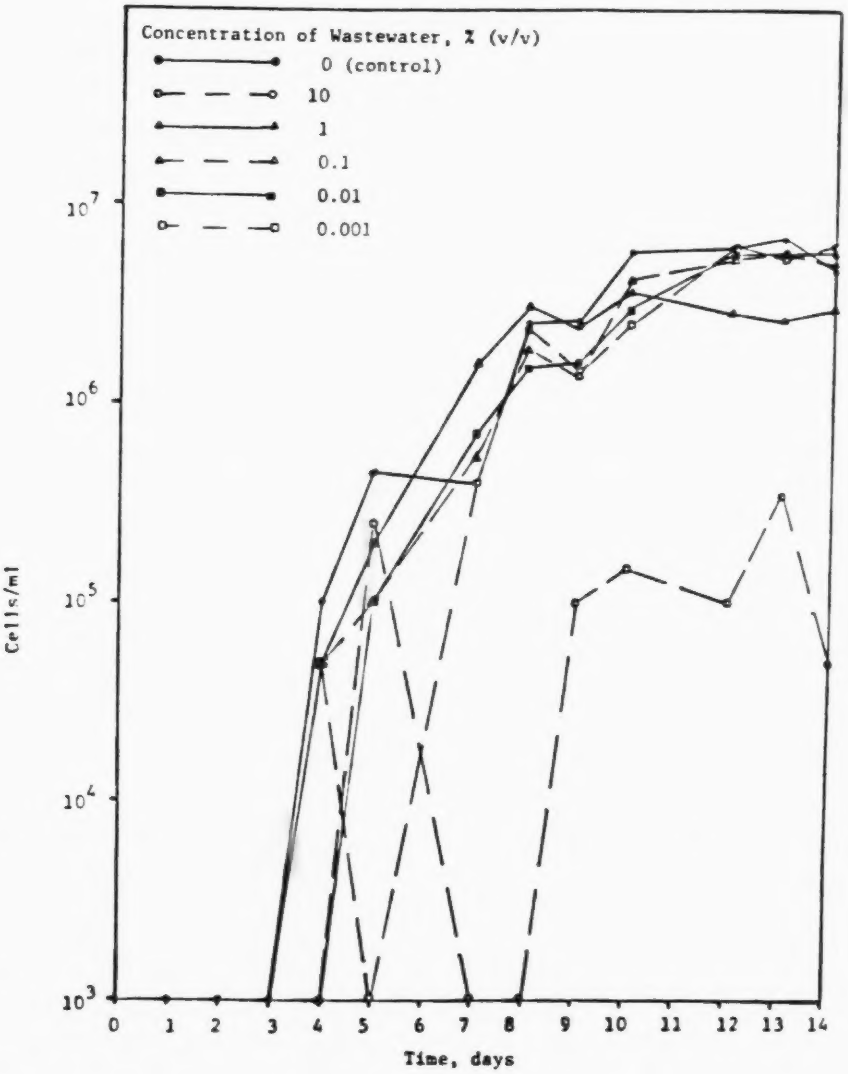


Figure M-1. Algal assay (rangefinding) of MSMA wastewater. (Data shown in Table M-1).

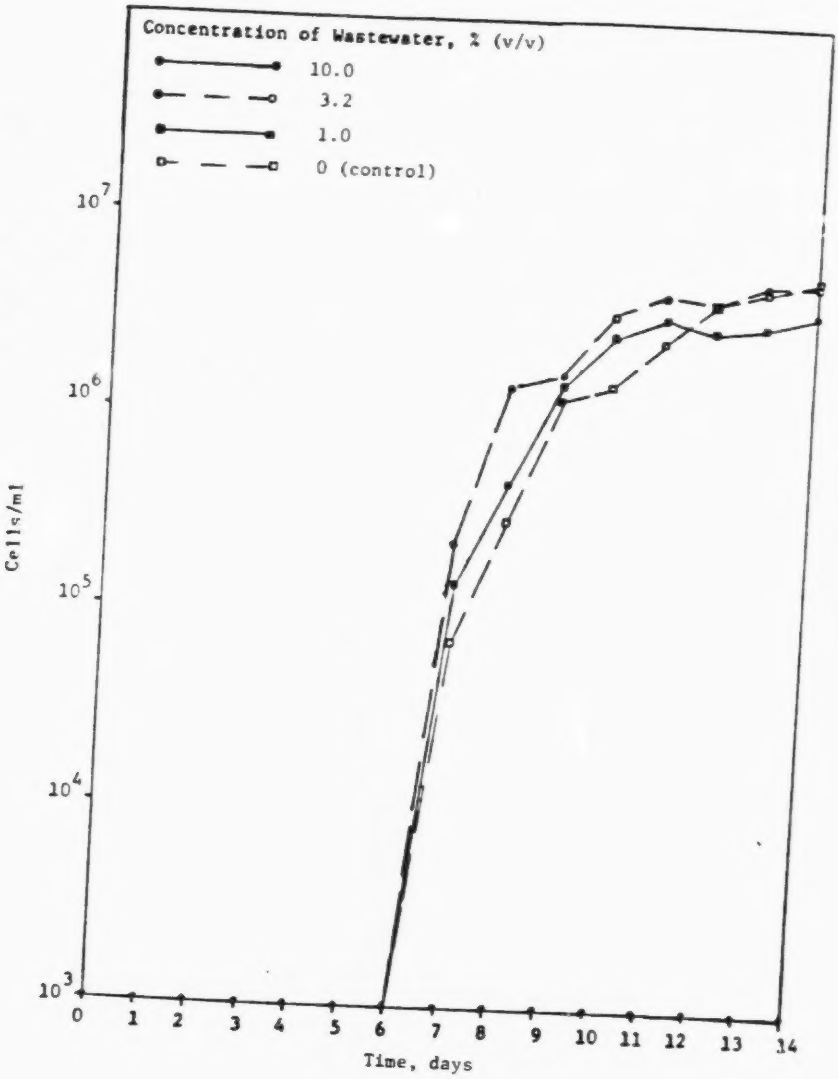


Figure M-2. Algal assay (narrow range) of MSMA wastewater. (Data shown in Table M-2).

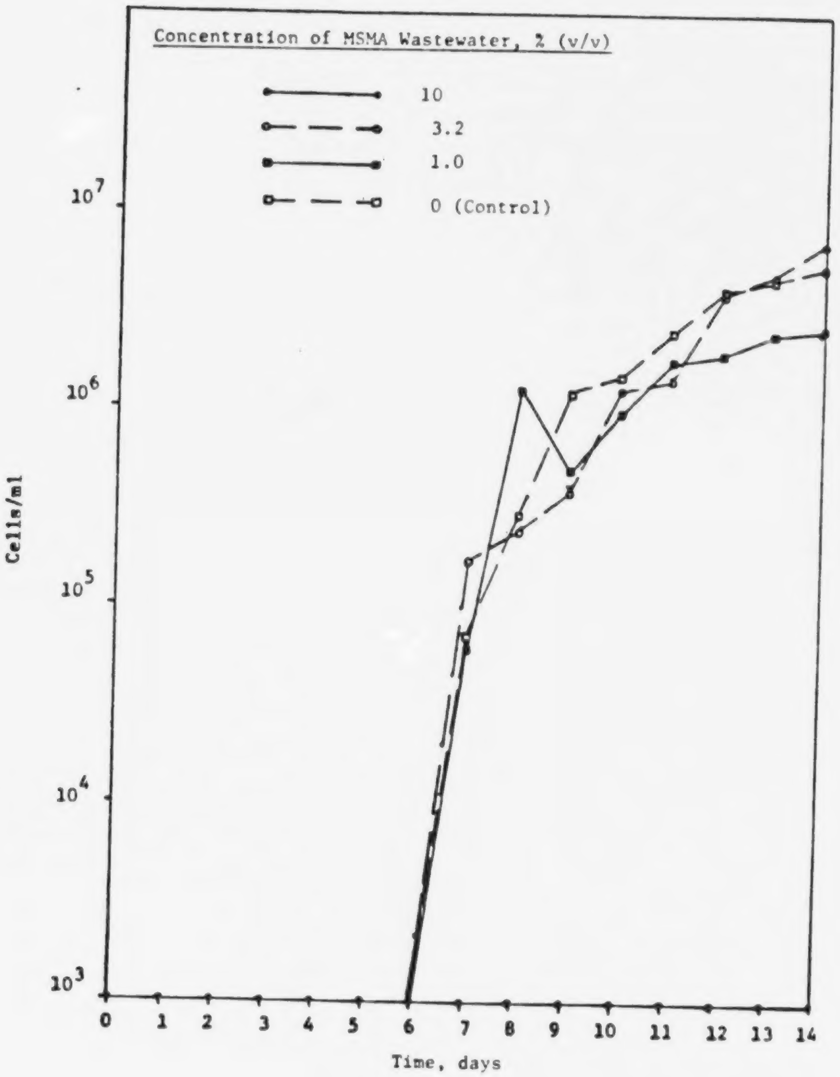


Figure M-3. Algal assay of GAC column-treated MSMA wastewater. (Data shown in Table M-5).

APPENDIX N

FISH AND ALGAL BIOASSAY DATA--MANEB WASTEWATER STUDIES

Table N-1. SCREENING TESTS OF TOXICITY TO FISH OF COMMERCIAL MANEB PREPARATION

Maneb, mg/l (Calculated)	Final pH	No. fish surviving at stated time (Initial = 3)			
		24 hr	48 hr	72 hr	96 hr
0	6.5	3	3	3	3
0.01	6.0	3	3	3	3
0.1	6.5	3	3	3	3
1.0	6.5	3	1	1	1
10.0	6.5	0	0	0	0

Table N-2. SCREENING TESTS FOR TOXICITY OF MANEB WASTEWATERS TO FISH

% Wastewater (v/v)	No. Fish Surviving at 96 hr. (Initial = 3)	
	Plant A Wastewater	Plant B Wastewater
0 (Control)	3	2
Raw Wastewater		
0.01	2	3
0.1	3	0
1.0	0	0
10.0	0	0
Filtered Wastewater		
0.01	3	3
0.1	3	2
1.0	1	1
10.0	1	1

Table N-3. SCREENING TESTS OF TOXICITY OF PLANT B WASTEWATER TO FISH

Sample	Wastewater Concentration % (v/v)	pH	No. fish surviving at 96 hr (Initial = 3)
Control	0	6.7	3
"	0	6.7	3
Raw wastewater	0.01	6.6	3
	0.01	6.7	2
	0.018	6.7	3
	0.018	6.8	3
	0.032	6.8	3
	0.056	6.8	2
	0.056	6.8	3
	0.056	6.8	3
	0.1	6.8	0
	0.1	6.9	0
	10.0	7.2	0
	10.0	7.2	0

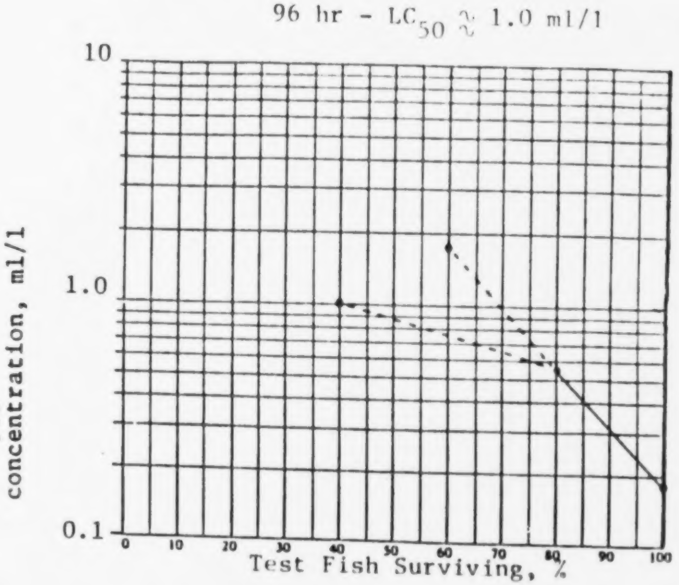


Figure N-1. 96 hr LC_{50} determination: maneb manufacturing wastewater, Plant A, unfiltered. (Data showin in Table 14-4).

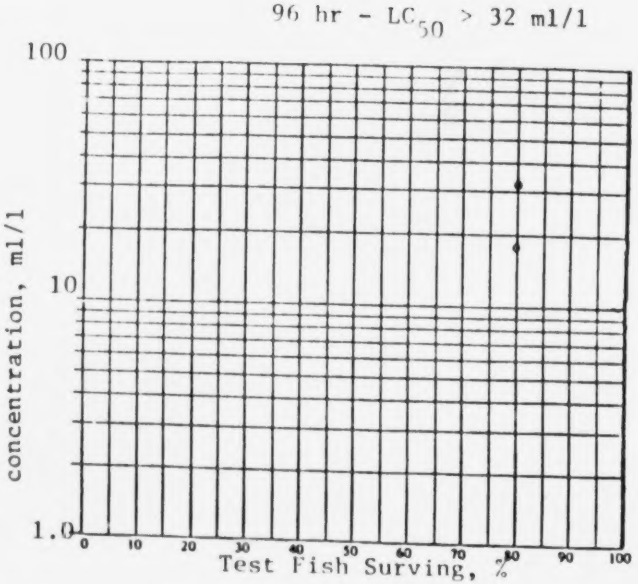


Figure N-2. 96 hr LC_{50} determination: maneb manufacturing wastewater, Plant A, filtered (What 2V). (Data shown in Table 14-4).

Table N-4. DETERMINATION OF LC$_{50}$ FOR FISH OF MANEB MANUFACTURING WASTEWATER (PLANT A)

Sample	Concentration, ml/l	Fish Surviving at 96 hr, % (Initial no. of fish = 10)
Control	0	100
Unfiltered Wastewater	0.18	100
	0.56	80
"	1.0	40
"	1.8	60
Filtered Wastewater		
	10	100
"	18	80
"	32	80

Table N-5. DETERMINATION OF LC$_{50}$ FOR FISH OF MANEB MANUFACTURING WASTEWATER (PLANT B)

Sample	Concentration, ml/l	Fish Surviving at 96 hr, % (Initial no. of fish = 10)
Control	0	100
Unfiltered Wastewater	0.1	70
"	0.32	0
"	1.0	0
Filtered Wastewater	5.6	100
"	10.0	0
"	18.0	0

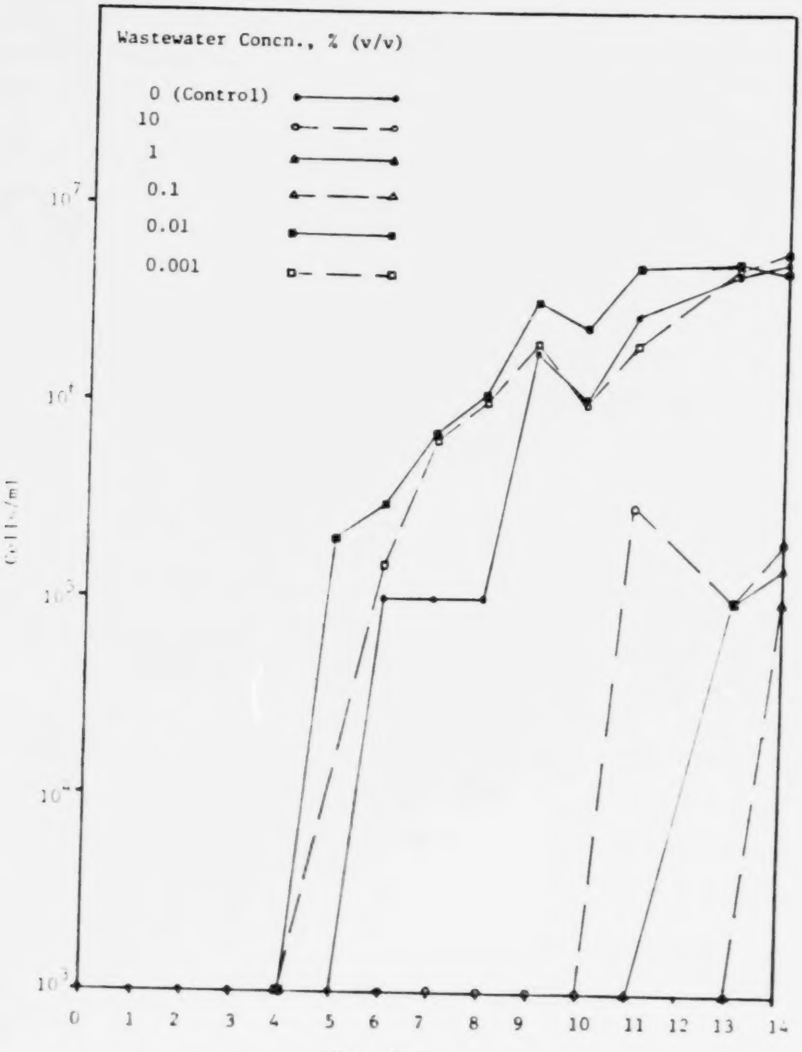


Figure N-3. Algal assay of Plant A wastewater. (Data shown in Table N-6).

Table N-6. EFFECTS OF FILTERED PLANT A WASTEWATER ON ALGAL GROWTH (RANGEFINDING) EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

	Growth, Percent of Control, in:				
	Plant A Wastewater Concentration, Percent (v/v)				
Time (days)	10	1.0	0.1	0.01	0.001
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	-	-	-	-
5	-	-	-	-	-
6	0	0	0	300	150
7	0	0	0	700	650
8	0	0	0	1100	1000
9	0	0	0	183	113
10	0	0	0	234	95
11	11	0	2	179	71
12					
13	2	2	1	115	107
14	4	3	2	91	112
15	0	0	1	115	102
16	0	0	1	96	98
17	0	0	0	125	112

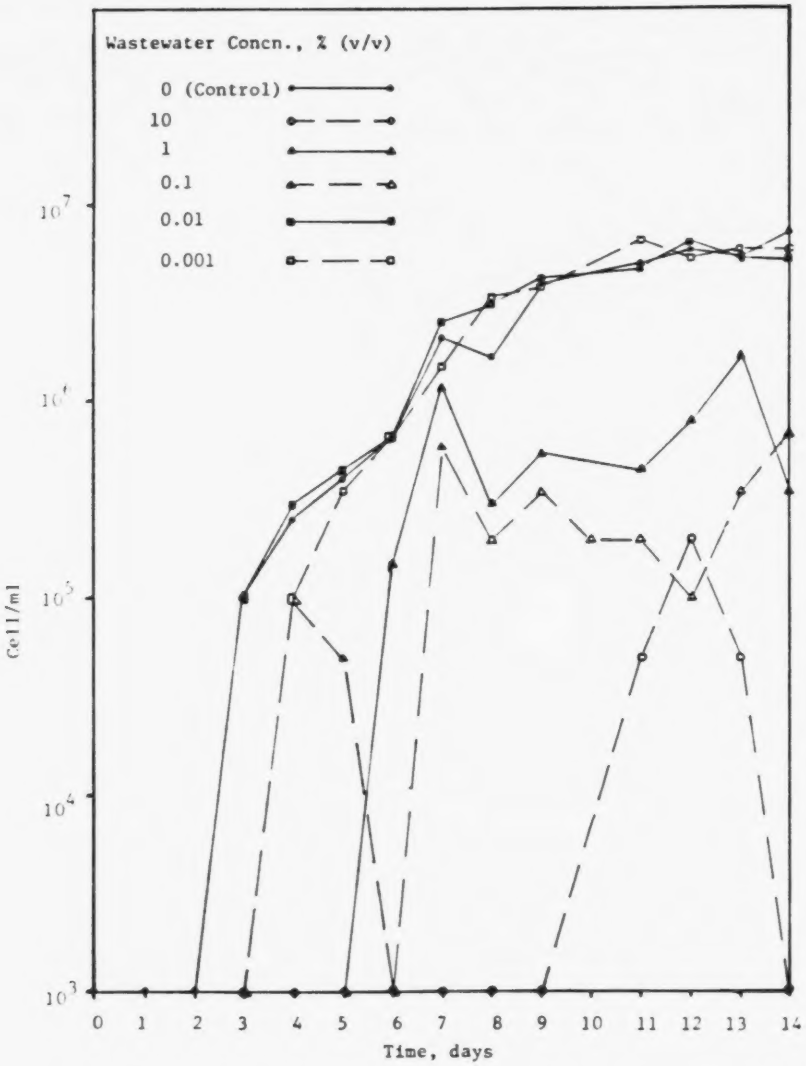


Figure N-4. Algal assay of Plant B wastewater. (Data shown in Table N-8).

Table N-7. EFFECT OF FILTERED PLANT B WASTEWATER SAMPLE 1 ON ALGAL GROWTH (RANGEFINDING) EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

Time (days)	Growth, Percent of Control, in:			
	Plant B Wastewater Concentration, Percent (v/v)			
	10	1.0	0.1	0.01
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	8	7	8	96
6	7	8	7	78
7	6	8	8	91
8	8	8	9	102
9				
10	7	7	9	92
11	7	9	10	113
12	7	8	8	110
13	7	8	7	110
14	6	7	8	97

Table N-8. EFFECTS OF FILTERED PLANT B WASTEWATER SAMPLE 2 ON ALGAL GROWTH (RANGEFINDING) EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

Time (days)	Growth, Percent of Control, in:				
	Plant B Wastewater Concentration, Percent (v/v)				
	10	1.0	0.1	0.01	0.001
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	-	-	-	-
5	0	0	40	120	40
6	0	0	13	113	88
7	0	23	0	100	100
8	0	57	29	121	71
9	0	18	12	190	200
10	0	14	9	104	99
11					
12	1	9	4	96	134
13	3	14	3	109	91
14	1	32	2	96	105
15	0	5	5	74	81
16	3	14	13	111	86
17	1	10	13	90	97
18	7	17	13	84	80

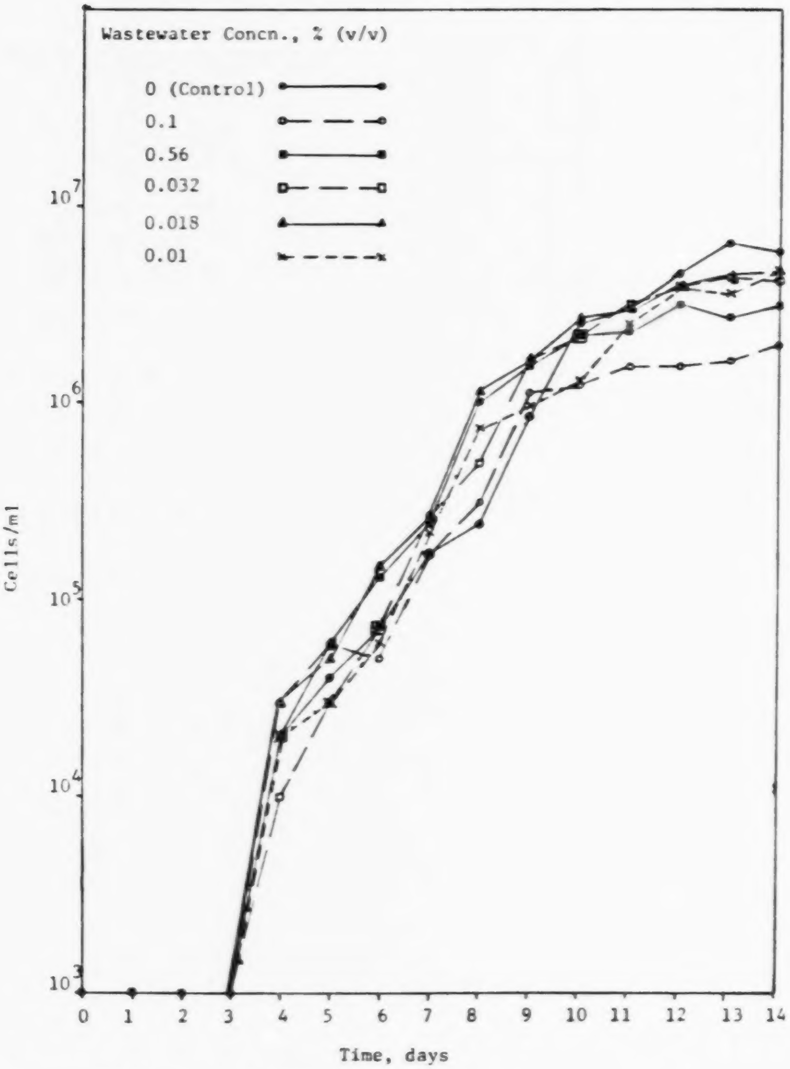


Figure N-5. Algal assay of Plant B wastewater.
(Data shown in Table N-9).

Table N-9. EFFECTS OF FILTERED PLANT B WASTEWATER SAMPLE 2 ON ALGAL GROWTH (NARROW RANGE) EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

Time (days)	Growth, Percent of Control, in: Plant B Wastewater Concentration, Percent (v/v) 0.1	0.056	0.032	0.018	0.01
0	-	-	-	-	-
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	150	100	50	150	100
5	150	150	75	125	75
6	140	185	100	214	86
7	100	141	147	159	129
8	129	416	204	479	304
9	135	184	196	195	117
10	98	174	174	210	106
11	49	75	102	95	82
12	34	70	86	88	86
13	25	42	66	67	56
14	34	54	70	79	83

Table N-10. EFFECT OF ACTIVATED CARBON TREATMENT ON TOXICITY OF MANEB WASTEWATERS TO FISH

Sample	Concentration ml/l	Fish Surviving at 96 hr, % (Initial no. of fish = 10)	LC$_{50}$, 96 hr. ml/l
Control dilution water (4 replicates)	-	100	
Plant A Wastewater			
Untreated	0.056	100	
	0.1	100	
	0.18	100	∿1
	0.56	80	
	1.0	40	
	1.8	60	
Filtered, Whatman 2V	10	100	
	18	80	>32
	32	80	
GAC treated	18	100	>32
	32	90	
Plant B Wastewater			
Untreated	0.1	70	
	0.32	0	∿0.18
	1.0	0	
Filtered, Whatman 2V	0.1	100	
	0.32	100	
	1.0	100	∿3.2
	10.0	0	
	18.0	0	
	32.0	0	
GAC Treated	0.32		
	1.0	100	
	3.2	90	
	10	90	
	18	80	>32
	32	60	(∿42)

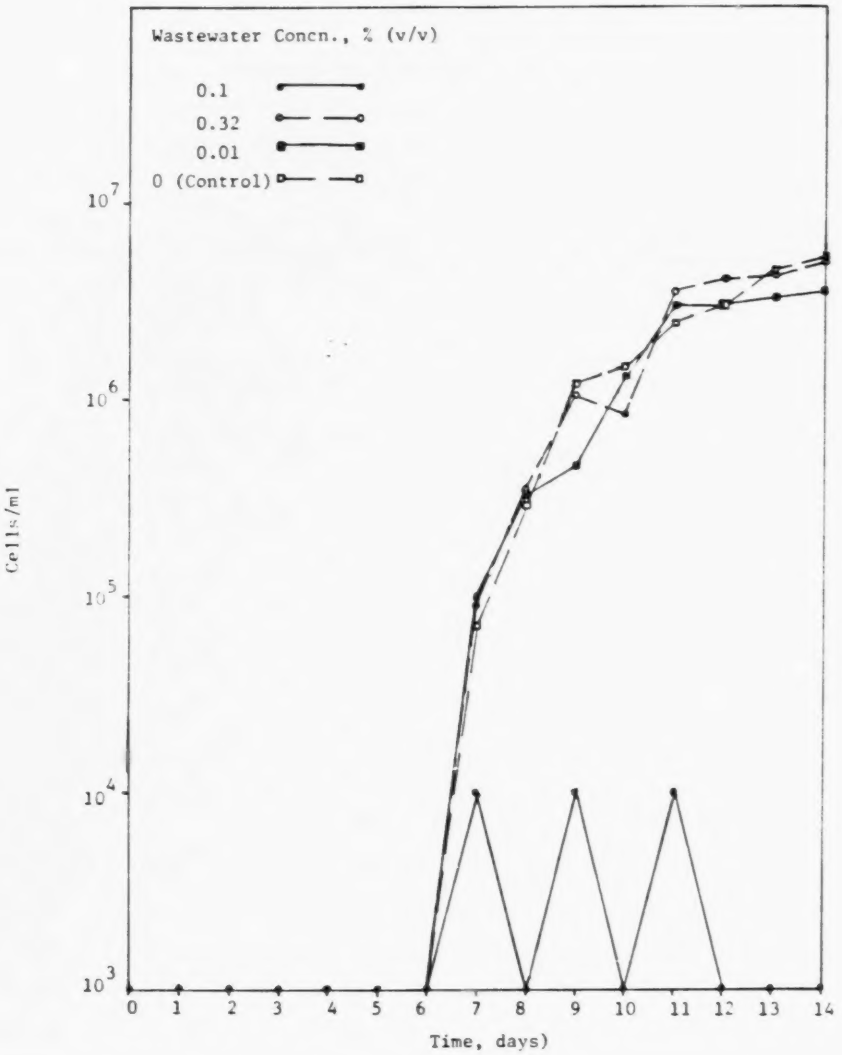


Figure N-6. Algal assay of Plant B wastewater, GAC treated. (Data shown in Table N-11).

Table N-11. EFFECT OF PLANT A WASTEWATER AFTER CARBON TREATMENT ON ALGAL GROWTH EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

	Growth, Percent of Control, in:		
	Plant A Wastewater Concentration, Percent (v/v)		
Time (days)	0.1	0.032	0.01
0	-	-	-
1	-	-	-
2	-	-	-
3	-	-	-
4	-	-	-
5	-	-	-
6	-	-	-
7	14	128	143
8	0	120	114
9	1	87	38
10	0	58	91
11	0	145	125
12	0	104	77
13	0	116	73
14	0	106	87
15	0	114	94
16	0	95	93
17	0	109	92

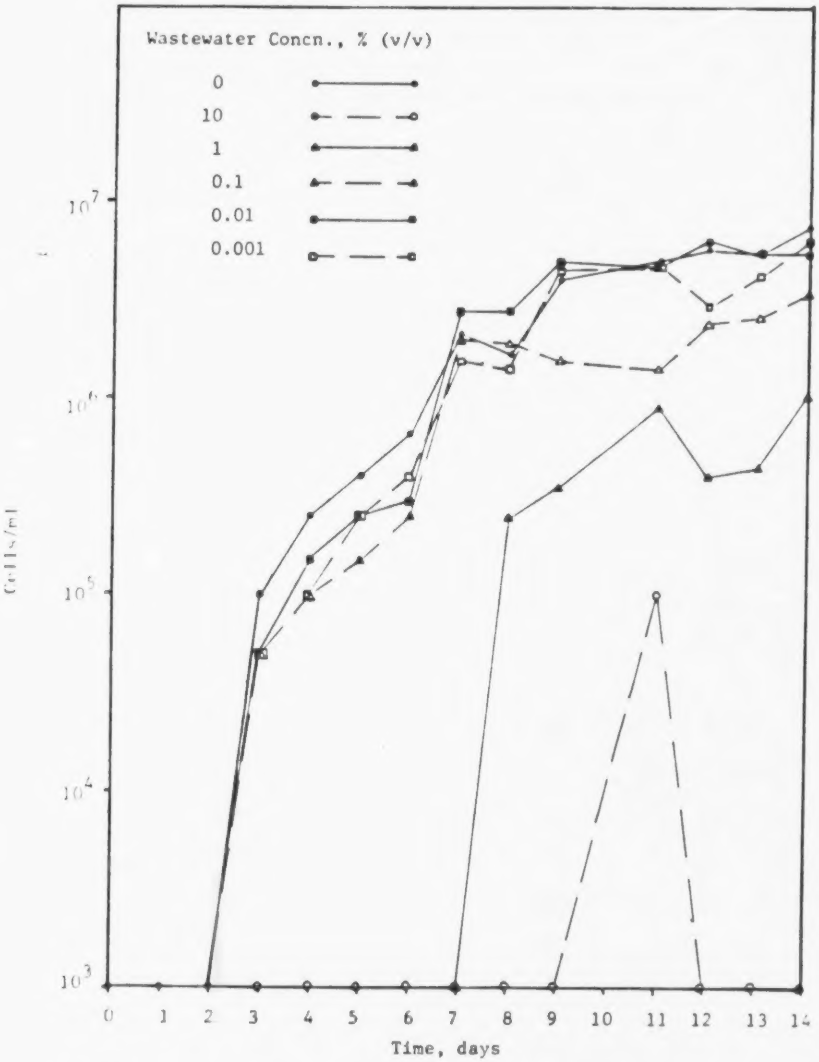


Figure N-7. Algal assay of Plant B wastewater, GAC treated. (Data shown in Table N-12).

Table N-12. EFFECTS OF PLANT B WASTEWATER AFTER CARBON TREATMENT ON ALGAL GROWTH (RANGEFINDING) EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

	Growth, Percent of Control, in:				
	Plant B Wastewater Concentration, Percent (v/v)				
Time (days)	10	1.0	0.1	0.01	0.001
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	0	0	50	50	50
5	0	0	40	60	40
6	0	0	38	63	63
7	0	0	38	46	62
8	0	0	98	131	74
9	0	15	115	167	85
10	0	9	39	124	110
11					
12	2	18	29	96	97
13	0	7	41	107	50
14	0	8	47	99	78
15	0	14	47	80	86
16	0	13	77	104	123
17	0	19	72	86	95
18	0	14	55	94	86

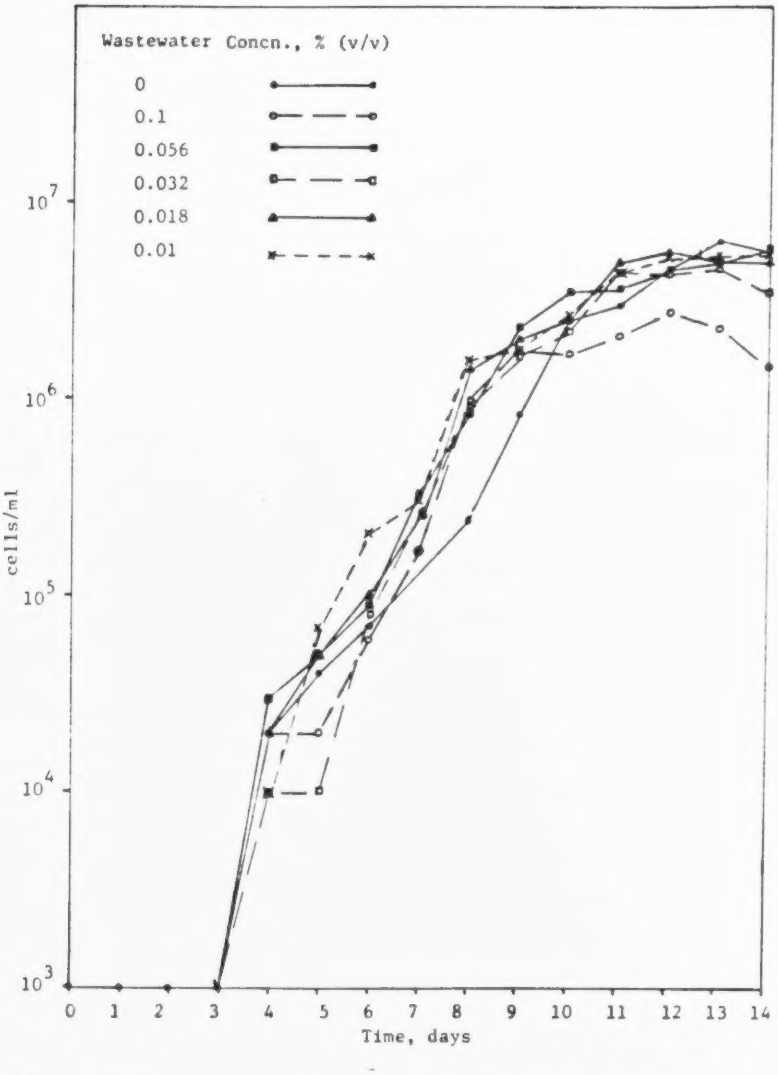


Figure N-8. Algal assay of Plant B wastewater, GAC treated. (Data shown in Table N-13).

Table N-13. EFFECT OF PLANT B WASTEWATER AFTER CARBON TREATMENT ON ALGAL GROWTH EXPRESSED AS PERCENTAGE OF ALGAL GROWTH IN CONTROL

	Growth, Percent of Control, in:				
	Plant B Wastewater Concentration, Percent (v/v)				
Time (days)	0.1	0.056	0.032	0.018	0.01
0	-	-	-	-	-
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	100	150	50	100	50
5	50	125	25	125	175
6	86	129	114	143	300
7	100	194	153	153	176
8	417	346	388	617	658
9	212	274	194	241	215
10	137	282	176	210	214
11	69	118	148	164	150
12	63	100	98	124	116
13	36	77	71	77	84
14	25	85	60	97	100
15					
16					
17	38	88	96	106	98
18					
19	28	70	71	79	84
20					
21					

Table N-14. EFFECT OF ACTIVATED SLUDGE TREATMENT ON TOXICITY OF MANEB WASTEWATERS TO FISH

Sample	ml/l	%, v/v	% Fish Surviving at 96 hr, (Initial no. of fish = 10)
Control, dilution water, replicate 1	-		100
Control, dilution water, replicate 2	-		90
Primary sewage			
Influent	100	10	100
	180	18	100
Effluent			
-Unit 1	180	18	90
-Unit 2	180	18	100
Primary sewage + 10% Plant A wastewater			
Influent	100	10	40
	180	18	70
Effluent			
-Unit 1	180	18	av. 70 { 90
-Unit 2	180	18	50
Primary sewage + 10% Plant B wastewater			
Influent	100	10	0
	180	18	0
Effluent			
-Unit 1	180	18	av. 45 { 60
-Unit 2	180	18	30

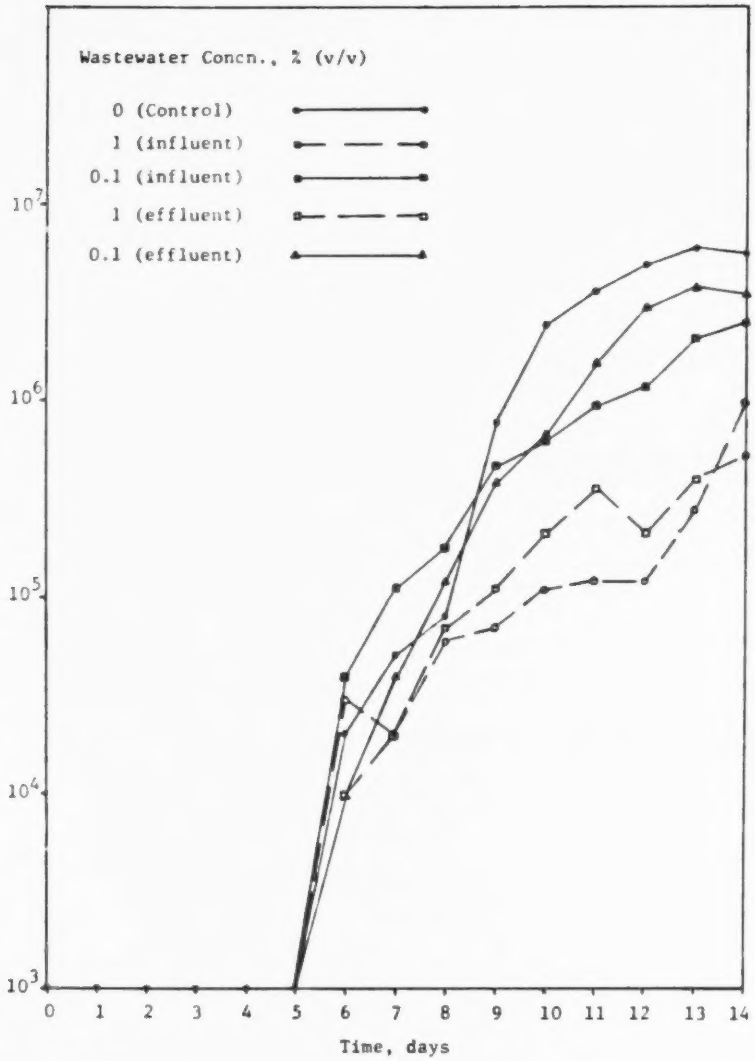


Figure N-9. Algal assay of influent and effluent of activated sludge units fed with Plant A maneb manufacturing wastewater (10%). (Data shown in Table N-15).

Table N-15. ALGAL ASSAY OF INFLUENT AND EFFLUENT OF ACTIVATED SLUDGE UNITS FED WITH PLANT A MANEB MANUFACTURING WASTEWATER (10%)

	Growth, Percent of Control, in					
	Influent Concn., % (v/v)			Effluent Concn., % (v/v)		
Time (days)	10	1.0	0.1	10	1.0	0.1
0	-	-	-	-	-	-
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	-	150	200	-	50	50
8	-	40	220	-	40	80
9	-	75	225	-	88	150
10	-	9	60	-	14	49
11	-	4	25	-	9	27
12	-	3	26	-	10	43
13	-	2	24	-	4	60
14	-	5	35	-	7	64
15	-	17	44	-	9	61

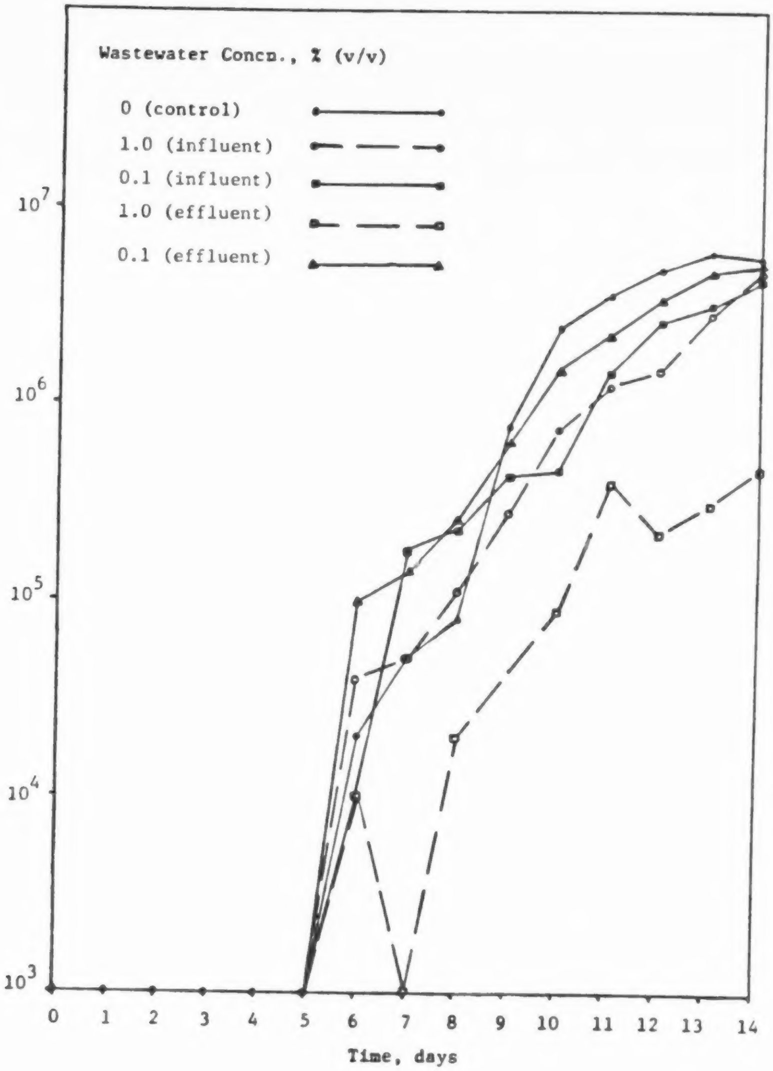


Figure N-10. Algal assay of influent and effluent of activated sludge units fed with Plant B maneb. (Data shown in Table N-16).

Table N-16. ALGAL ASSAY OF INFLUENT AND EFFLUENT OF ACTIVATED SLUDGE UNITS FED WITH PLANT B MANEB MANUFACTURING WASTEWATER (10%)

Growth, Percent of Control, in

Time (days)	Influent Concn., % (v/v)			Effluent Concn., % (v/v)		
	10	1.0	0.1	10	1.0	0.1
0	-	-	-	-	-	-
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	-	200	50	-	50	500
8	-	100	360	-	-	280
9	-	138	288	-	25	325
10	-	36	56	-	14	82
11	-	31	19	-	4	61
12	-	35	41	-	4	63
13	1	31	54	-	4	71
14	-	48	54	-	5	79
15	-	86	85	-	8	94

APPENDIX O

TESTS OF EFFECTS OF PESTICIDE WASTEWATERS ON DOMESTIC SEWAGE ORGANISMS: SPOT TESTS

Table 0-1. EFFECTS OF PESTICIDE WASTEWATERS IN SPOT TESTS

	Zone of Inhibition, mm				
	Wastewater Concentration, %				
Test Sample	100	10	1.0	0.1	0.01
Atrazine wastewater	0	0	0	0	0
-GAC treated	0	0	0	0	0
-Breakthrough from GAC column	0	0	0	0	0
Oryzalin wastewater	2	0	0	0	0
-GAC treated	0	0	0	0	0
-Breakthrough from GAC column	0	0	0	0	0
Oryzalin washwater	3	0	0	0	0
MSMA wastewater-grab sample	0	0	0	0	0
MSMA wastewater	0	0	0	0	0
Maneb wastewater, Plt A					
-Grab	2[1]	0[2]	0	0	0
-Composite, untreated	2	0	0	0	0
-Composite, GAC treated	1-2	0	0	0	0
Maneb wastewater, Plt B					
-1st sample	2-3	0	0	0	0
-2nd sample	2	0	0	0	0

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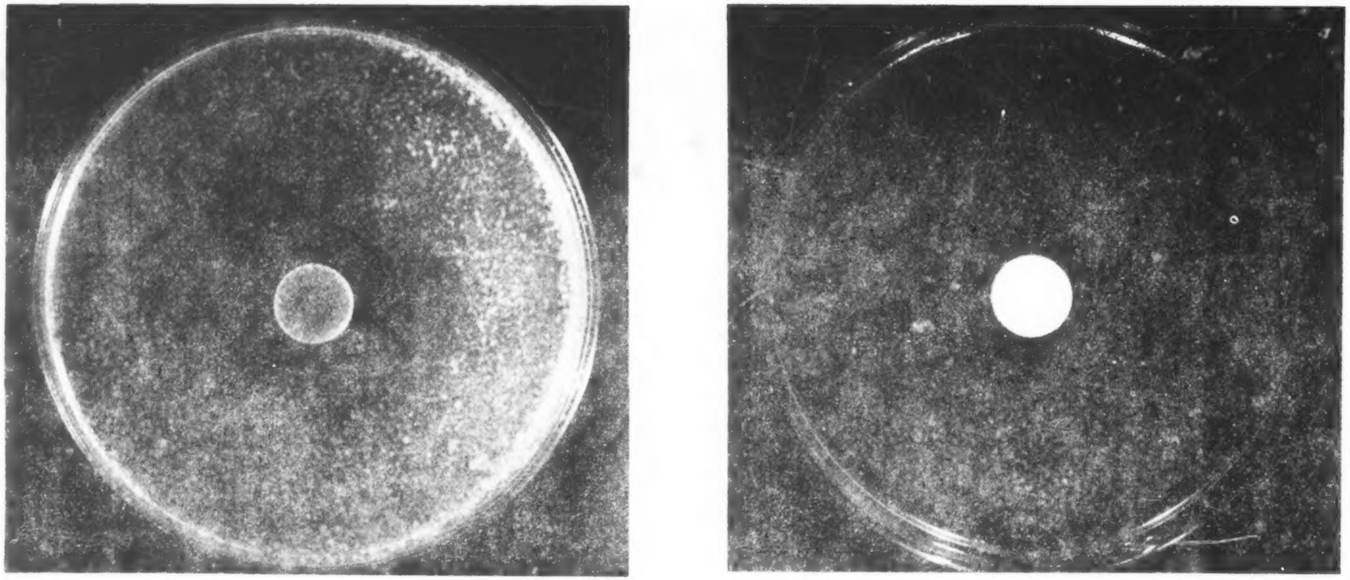
[1] A second zone surrounding the first with colonies of reduced size was 6 mm wide

[2] No clear zone existed but a zone 4-5 mm wide was present with colonies of reduced size.



a) Oryzalin Wastewater, Undiluted

b) Oryzalin Washwater, Undiluted

Figure O-1. Spot tests showing toxicity of oryzalin wastewater and washwater to domestic sewage flora.

APPENDIX P

OXYGEN UPTAKE STUDIES WITH PESTICIDE WASTEWATERS

Figures in Appendix P present data on the O_2 uptake studies performed on pesticide wastewaters at various concentrations. Standard procedure was followed as described in Section 3. Conditions tested were as follows:

Tapwater - 270 ml tapwater + 30 ml sludge

Sewage - 270 ml sewage + 30 ml sludge

10% Pesticide - 240 ml sewage + 30 ml sludge + 30 ml wastewater

1% Pesticide - 267 ml sewage + 30 ml sludge + 3 ml pesticide.

The tests are only moderately predictive of later results with activated sludge units since the process of acclimitization cannot be expected to occur with fresh sludge within the time limits of this test. Additionally the test may give false positives where chemical oxidation occurs, a possibility with some industrial wastewaters. At the least, however, this test can indicate concentrations showing gross toxicity.

While *ex post facto* interpretation can be overdone given the gift of hindsight, certain patterns emerged from the oxygen uptake studies which foreshadowed the results of the biological treatability efforts. As shown in Figures P-1 and P-2 MSMA and atrazine wastewater showed a pattern of non-interference with bacterial processes. On the other hand, at 10% concentration, oryzalin wastewater caused marked inhibition (Figure P-3). At 1%, oryzalin wastewater caused much less inhibition, at least over the duration of the test. It will be remembered, however, that 1% oryzalin eventually disrupted the activated sludge process.

The results with maneb were more ambiguous (Figures P-4 and P-5). Plant B wastewater was only moderately inhibitory at 10% concentration

The oxygen uptake studies are of little predictive value for the biological treatability of the pesticide component of the wastewater. While the pesticide may not interfere with bacterial processes as is the case with MSMA and atrazine wastewaters, it cannot be assumed that the pesticide is amenable to biological degradation.

The oxygen uptake study, therefore, must be seen as a companion measure which can provide for more intelligent use of the pilot activated sludge systems, but cannot substitute for this process.

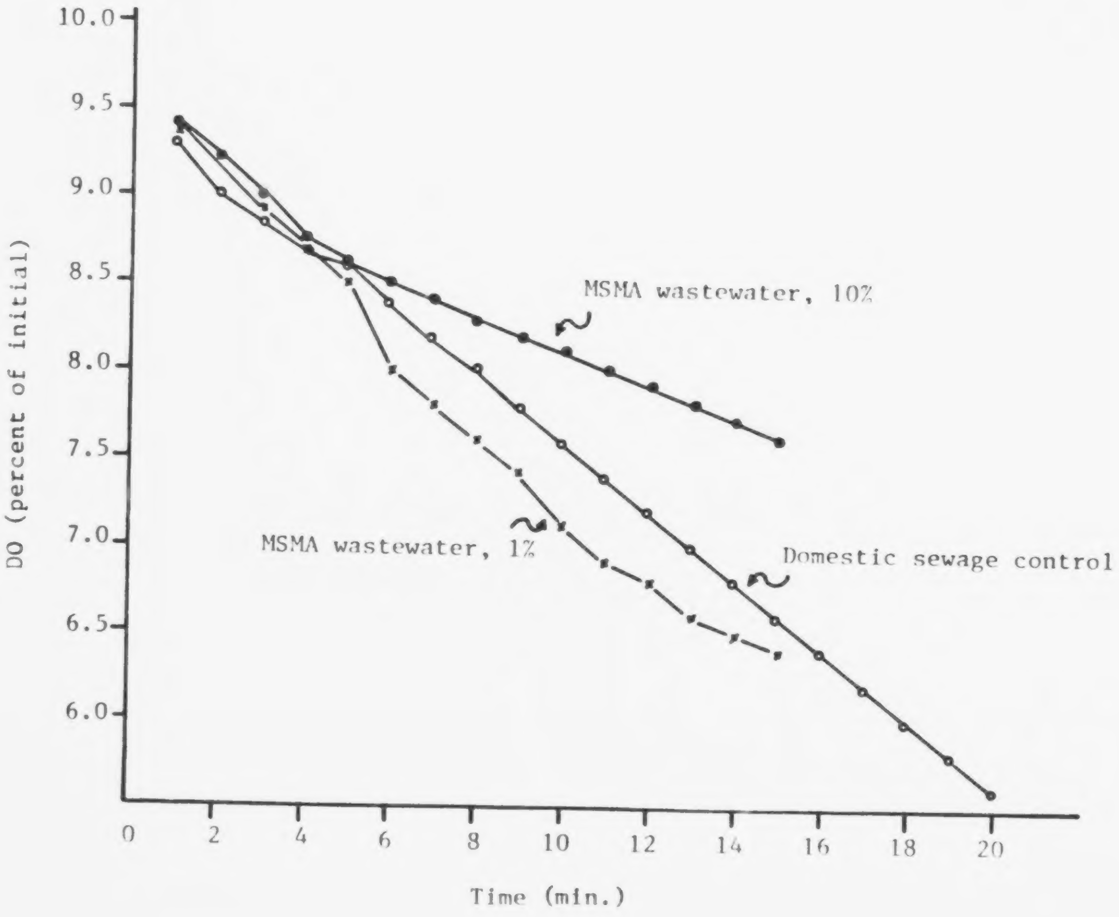


Figure P-1. Oxygen uptake studies with MSMA wastewater

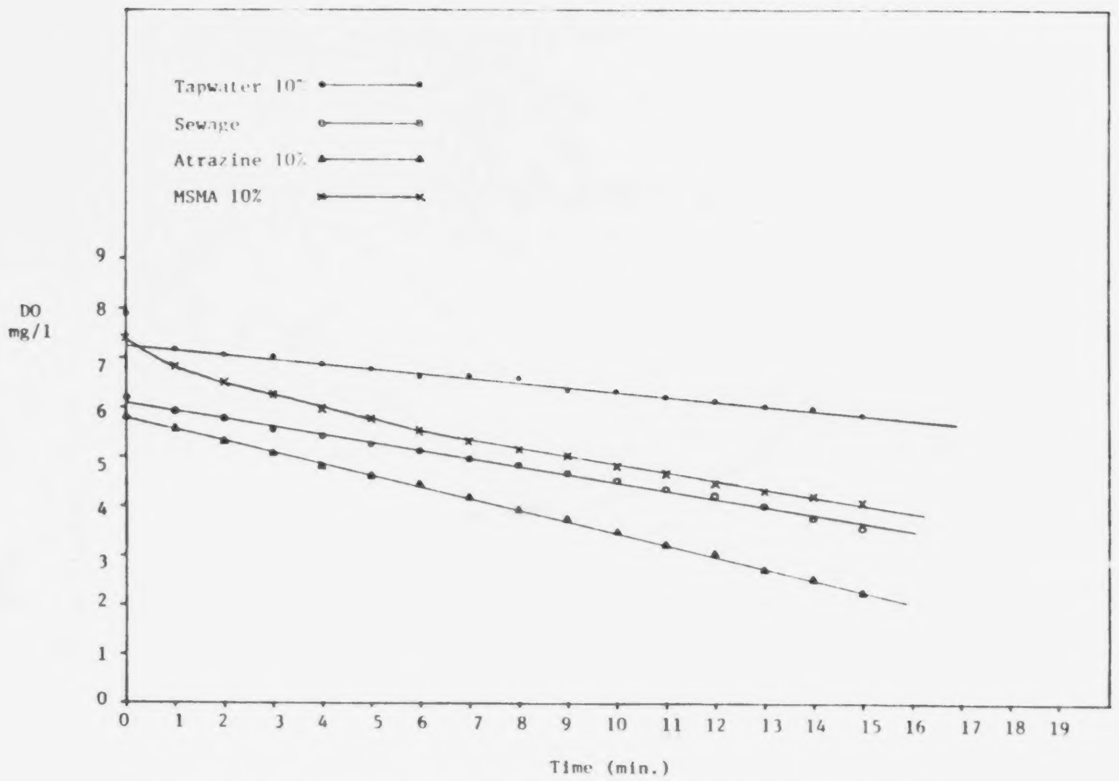


Figure P-2. Oxygen uptake studies of atrazine wastewater.

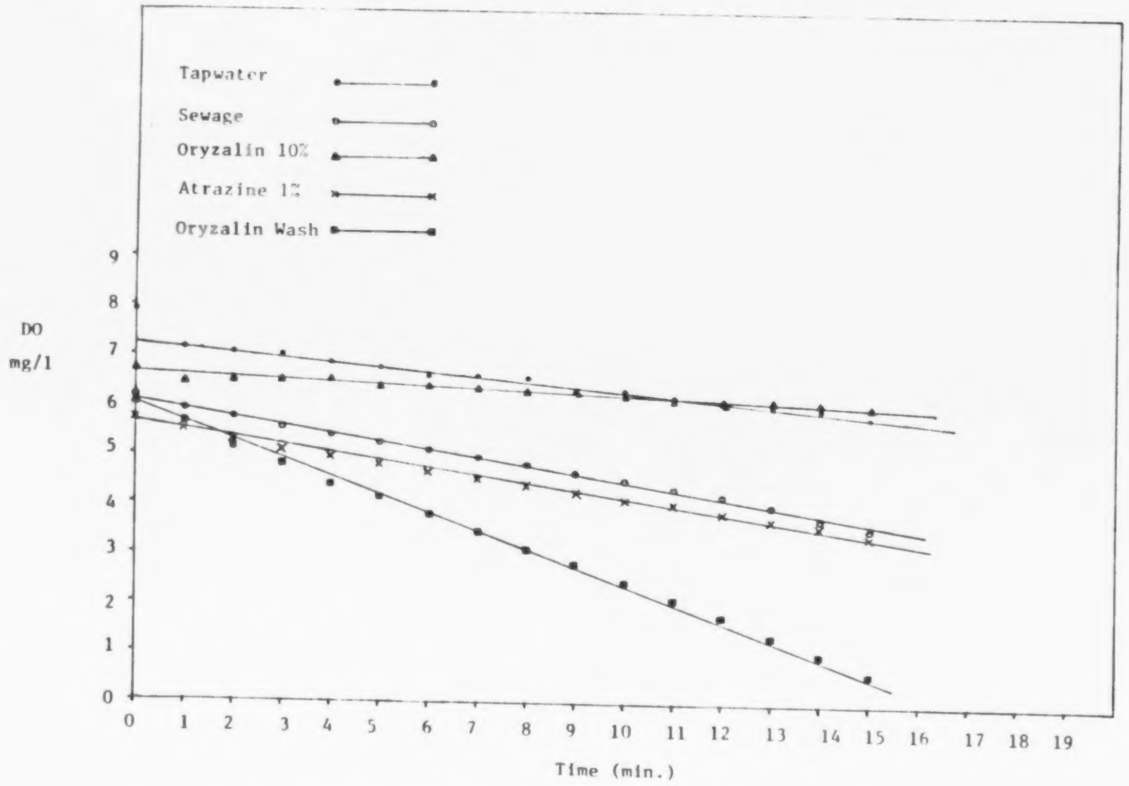


Figure P-3. Oxygen uptake study of oryzalin wastewater.

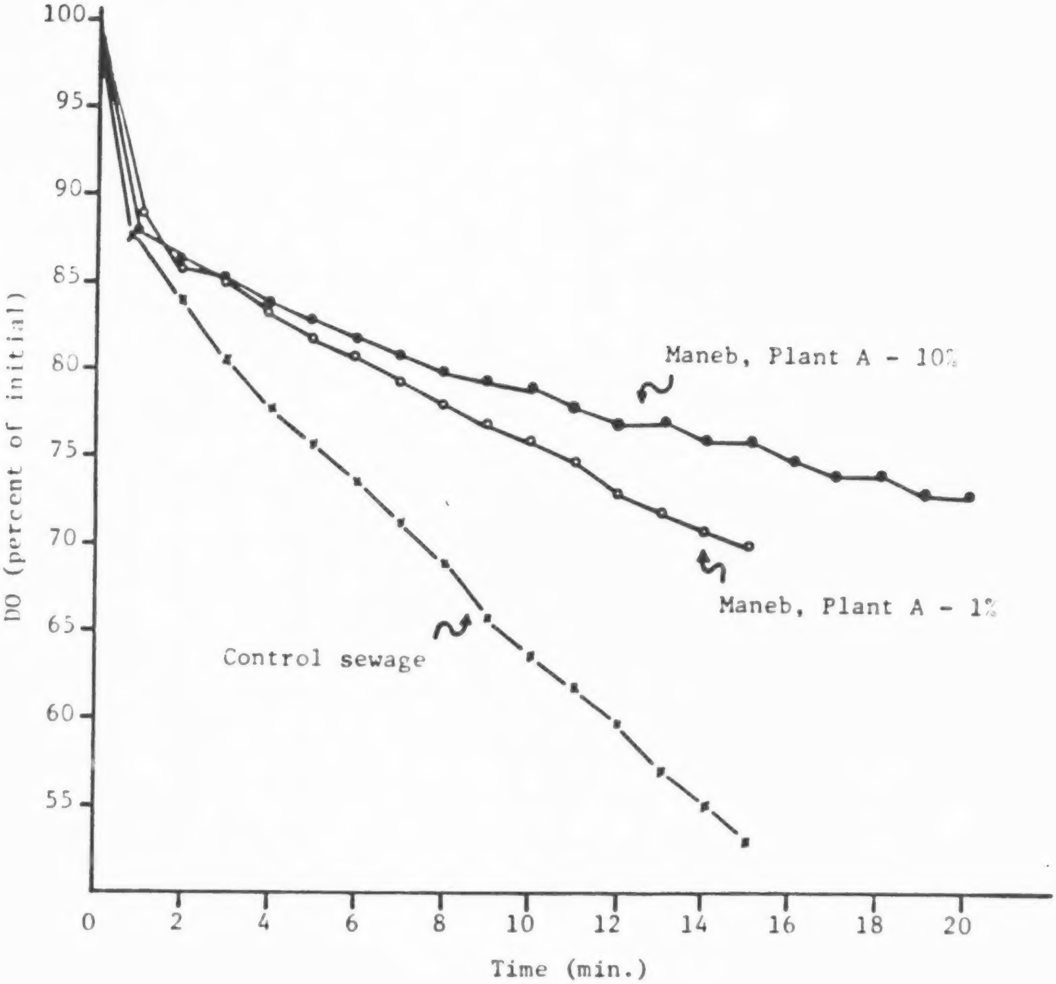


Figure P-4. Oxygen uptake study with maneb wastewater - Plant A.

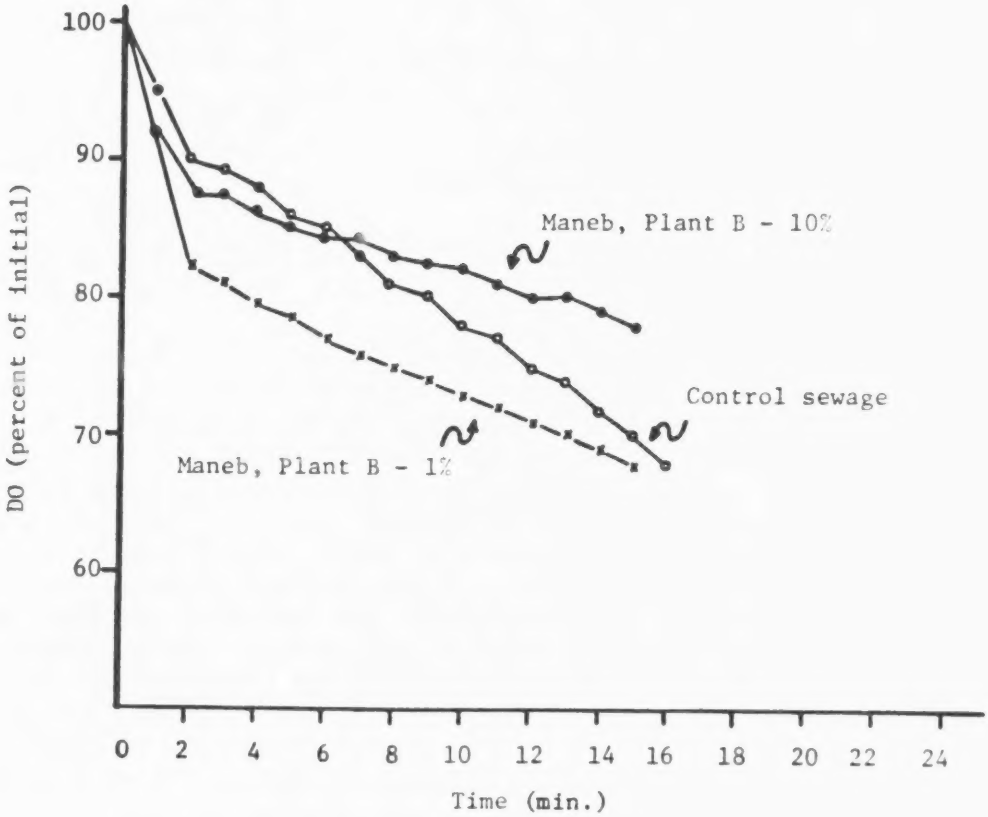


Figure P-5. Oxygen uptake study with maneb wastewater - Plant B.